THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

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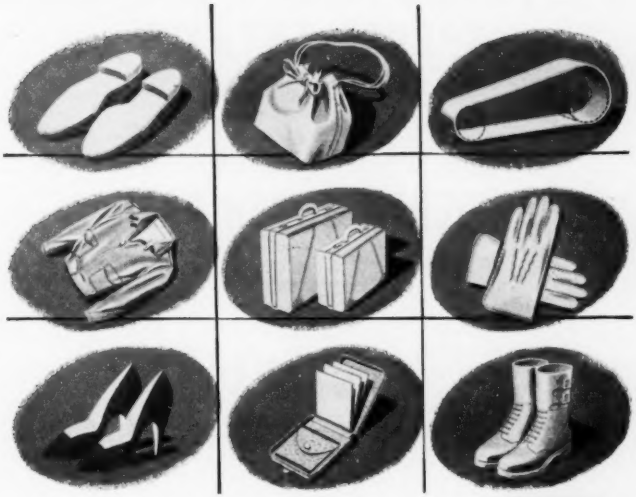

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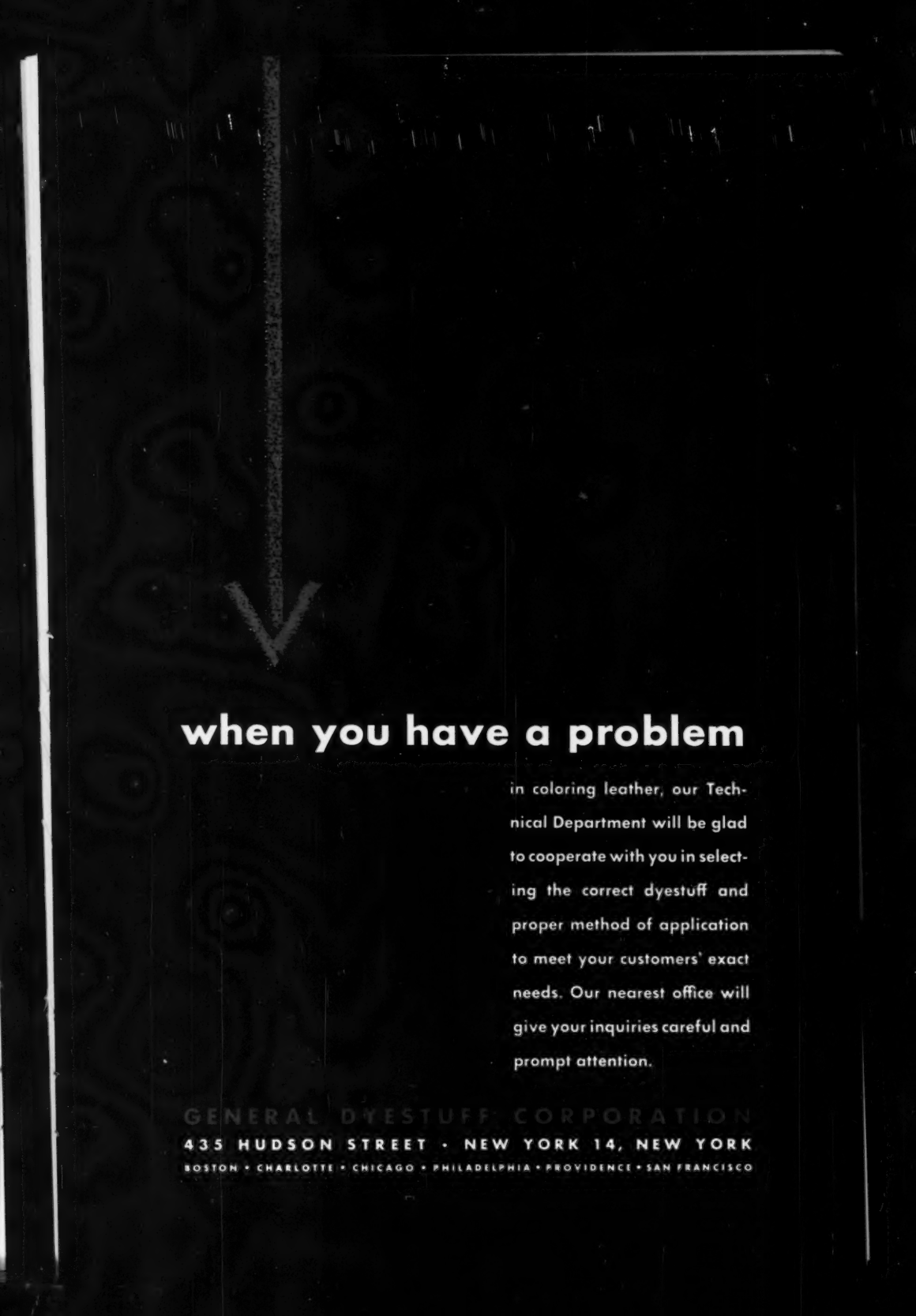

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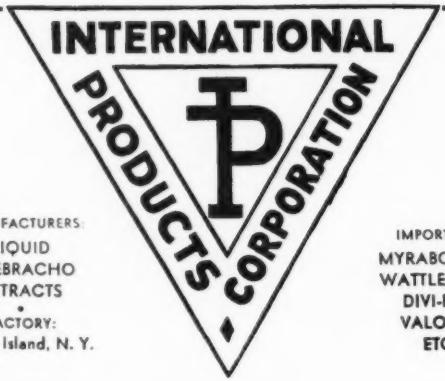

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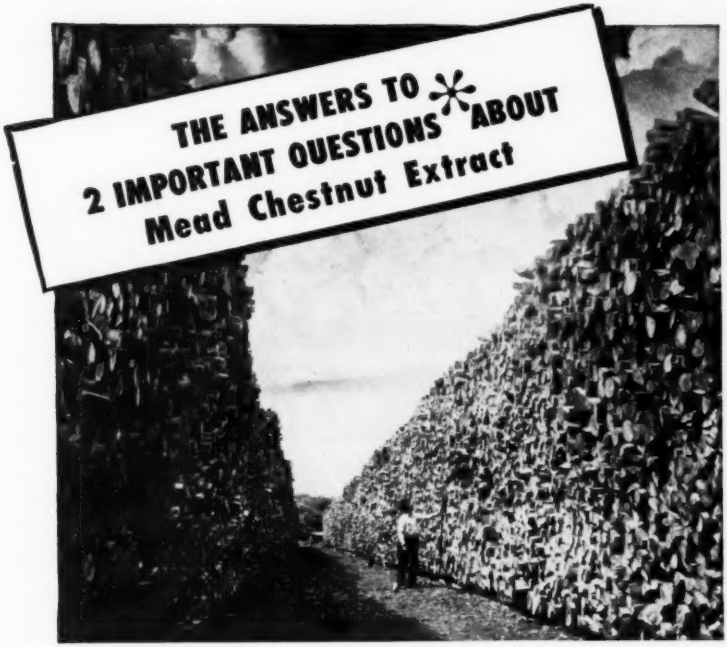

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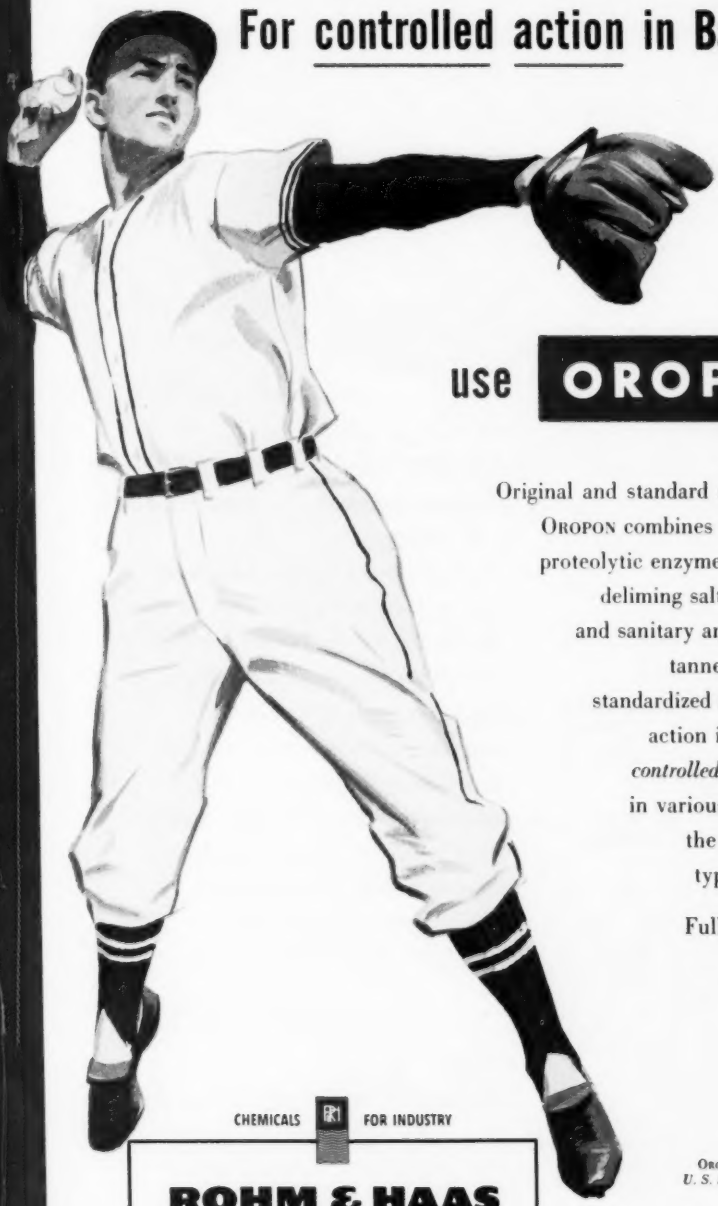

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VOL. XLVII SEPTEMBER 1952 No. 9

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SECRETARY'S NOTICE

We are advised that the International Union of Leather Chemists Societies will meet in Barcelona, Spain. The exact dates in September 1953 are not yet available.

Any member who desires to submit or present a paper at this meeting is requested to advise Dr. H. G. Turley who is the delegate to this meeting. Please advise at once if you desire to submit a paper.

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WALTER C. BUETHE

Walter C. Buethe, an active member of the Association since 1946 and long associated with the Rohm & Haas Leather Chemicals Sales Department, died after a brief illness on June 26, 1952. Following graduation from the University of Wisconsin in 1927, Mr. Buethe devoted most of his career to activities connected with the leather industry. Joining the Rohm & Haas Company in 1929, he became well known to tanners in the Mid-West and New England where he engaged in sales and demonstration work with leather chemicals. During recent years, he has been Acting Head of the Leather Chemicals Sales Department of the Rohm & Haas Company with headquarters in Philadelphia.

Mr. Buethe was one of the first members of his organization to join the armed forces during World War II. Over a five year period he saw service with the Army in Iceland, Africa, Great Britain, and Germany, attaining the rank of Major.

All of those who were fortunate enough to have been associated with Mr. Buethe will remember him as an able co-worker and a true friend.

MINUTES OF THE MEETING OF THE SUPERVISORY COMMITTEE ON TANNIN ANALYSIS

A meeting of the Tannin Analysis Supervisory Committee was held at the New Ocean House, Swampscott, Massachusetts on June 1, 1952. The meeting was called to order by Chairman G. W. Stanbery at 2 P. M. The following members and guests were present: J. H. Davis, A. N. Kay, R. L. Moore, F. F. Marshall, E. E. Presley, J. S. Rogers, G. W. Stanbery, C. G. Telander, J. F. Wagoner, I. D. Clarke, F. P. Luivsi, M. L. Happich, F. L. Hilbert, and D. Williams.

The minutes of the last meeting held at Philadelphia, Pennsylvania were approved as published in the May Journal. A letter from Mr. C. A. Blair was presented in which he requested that his privileges as a member to vote and enter into discussions be given to his son, T. C. Blair at this meeting.

Chairman, Stanbery then turned the meeting over to A. N. Kay, Chairman of the Subcommittee on the Revision of the Methods. After considerable discussion, agreement was reached on all of the details pending in the revision of the methods. Mr. Kay is now going to draw up the final draft of the methods incorporating the revisions agreed upon and submit it to the members for final approval. The question of changing the now specified use of salt for preserving sheep skins for color tests to borophenol was discussed from the point of view of whether it was a "change in detail" or "change in methods". Mr. Telander was requested to obtain an opinion from Council. Mr. Kay raised the question of our present allowance of .375 to .425 g. tannin per 100 ml. in extract analyses. He had submitted data on chestnut extract indicating the allowance to be too great. He suggested that committee work be undertaken on the subject but there was a lack of interest so the matter was tabled.

Mr. Stanbery expressed his appreciation and that of the Committee to Mr. Kay for his efforts in rewriting the methods. Mr. Stanbery also informed the Committee that his term as Chairman of the Committee terminates with this meeting. Council will appoint his successor. Mr. Telander tendered his resignation as Secretary of the Committee.

The meeting adjourned at 5:30 P. M.

J. F. WAGONER, *Acting Secretary.*

MINUTES OF MEETING OF THE STANDARDS AND SPECIFICATIONS COMMITTEE

New Ocean House, Swampscott, Massachusetts

JUNE 1ST, 1952

Members present: Ashcraft, Kay, Knight, Lollar, Mann, Presley, Witherell, and Telander, Chairman.

Meeting convened at 8:00 P. M.

R. Lollar presented a study of the precision of methods for analysis of leather as applied to chrome, vegetable retan upper leather. This study was based on collaborative work performed by seven laboratories and seven tanneries. The study indicated a relatively low degree of precision in the more important determinations, such as hide substance, grease and moisture. Dr. Lollar advocated the inclusion of a statement in the methods of the precision in the analytical methods. The Committee considered the report to be of great importance and recommended that it be brought to the attention of Council. It is to be recommended to Council that the matter be studied with the point of view of trying to discover the sources of error, and steps to be taken for their elimination.

S. Dahl, National Bureau of Standards, was recommended as member to replace E. Serfass, who has resigned from the committee.

The Chairman reported on the progress of KK-L-311, Section 6,000, Chemical Analyses. All suggestions and recommendations by this committee have been forwarded to the Federal Specifications Board and have been accepted as far as is known.

A request by Mr. Ashcraft to have the hide substance limits in KK-L-261-c, Class 3-4, Type #1, changed from 30-42% hide substance to 32-44% was discussed by the committee through correspondence and the majority of the committee members have agreed to the proposed change. It has been suggested that this matter was not within the scope of this committee. The Chairman was delegated to forward this request to Tanners' Council with the committee's recommendation.

The A.L.C.A. Tannin Analysis Committee is completing the revision of the tannin analysis methods. It was recommended that the final revision of the tannin analysis committee should be included in the pending revision of KK-L-311, Section 7,000, Tannin Analysis Methods. Since this work is largely editorial, the Chairman was delegated to include these recent revisions of the tannin analysis committee in Section 7,000 and forward it to the Federal Specifications Board with the committee's recommendation.

Specification KK-L-311, Section 60, Sampling and Acceptance Procedure, was discussed in detail. The change in sampling from three sampling positions to one position brought forth considerable criticism and discussion from the sole leather representatives on the committee. It was pointed out that the work done as basis for the change did not include sole leather. The results on which the recommendation for change were made are therefore not applicable to sole leather. It was also held forth that the generally accepted standard sampling procedure of the sole leather industry should be the basis irrespective of any other sampling which may be found preferable for other types of leather. The suggestion that a factor can be established which will convert results of chemical analyses based on the one sampling position to that of the three sampling positions was regarded by the sole leather representatives as being unsatisfactory and highly inaccurate. In the opinion of the committee, Section 60 needs clarification in several aspects in the definition of Sampling and Testing Procedure of "Finished Leather Articles". It was moved and seconded that Section 60 of KK-L-311 be rejected by the committee. The motion was carried, two members abstaining from voting. The Chairman expressed regrets that the committee was unable to agree with the recommendations of the Federal Specifications Board. He pointed out that this was the first instance in which agreement could not be obtained.

The meeting adjourned at 11:00 P. M.

CARL G. TELANDER, *Chairman*
A. L. C. A. Standards and
Specifications Committee.

COUNCIL MEETING MINUTES
THE AMERICAN LEATHER CHEMISTS ASSOCIATION

JUNE 1, 1952

New Ocean House
Swampscott, Massachusetts

The meeting convened at 8:00 P. M. Those present were Messrs. Robert M. Koppenhoefer, Harold G. Turley, Carl G. Telander, J. Stanley Kirk, Robert B. Hobbs, John Teas, and Fred O'Flaherty.

The minutes of the meeting of February 27th were read and received final approval.

Council approved a special local registration fee for daily attendance at the meeting.

Favorable reaction was evidenced for the 1953 meeting, the fiftieth anniversary of the A.L.C.A., to be at Cincinnati, if suitable dates are obtainable. Also to have the Wisconsin Tanners' Production Club sponsor one session.

Council approved making Messrs. Caspar Drueding and Thomas Faust life members.

Council voiced approval of having the meeting for 1954 in Philadelphia, and asking the Delaware Valley Group to conduct one session.

Mr. Telander reported for the Tannin Analysis Committee. A more detailed report will be made at the June 3rd Council meeting.

Mr. Wagoner requested that his committee on Industrial Waste Disposal be increased. He suggested Messrs. Presley and Harnly. Mr. Wagoner was advised to decide and Council would approve.

Dr. O'Flaherty reported that Mr. Frank Marshall has agreed to the instrument prepared by the Association counsel. He will return same, with minor changes, in the near future.

The following were appointed as the nominating committee: Mr. Robert Adams, chairman; Mr. A. C. Fleisch; Mr. David Wilson.

The meeting was adjourned at 9:00 P. M.

COUNCIL MEETING MINUTES
THE AMERICAN LEATHER CHEMISTS ASSOCIATION

JUNE 4, 1952

New Ocean House
Swampscott, Massachusetts

The meeting convened at 2:00 P. M. Members present were President Harold G. Turley, President-Elect Edwin Flinn, Council Members R. H. Hobbs and F. Leslie Collins, Secretary Fred O'Flaherty, visitors Messrs. John Teas, J. S. Kirk, and C. G. Telander.

Matters pertaining to the Technical Committees are to be transferred to Dr. Flinn. Dr. Flinn will go to Philadelphia and spend a day with Dr. Turley to arrange this. A report on the Technical Committee will then be prepared by Dr. Flinn.

Council accepted the resignation of Mr. G. Stanbery as chairman of the Tannin Analysis Committee. The Secretary is to confirm and express appreciation for five years of conscientious service.

Council appointed Mr. Arthur Kay as chairman of the Tannin Analysis Committee.

Council approved the additional members for the Industrial Waste Disposal Committee to assist Mr. J. F. Wagoner chairman; Messrs. E. E. Presley, W. C. Curtin, G. A. Butz, E. Thorstensen, and F. O'Flaherty.

The formation of a new committee on Mechanical Leathers was approved by Council. Mr. Alfred S. Berens was appointed chairman of this committee. He is to organize his committee and submit through Dr. Flinn a list of members and the proposed program of the committee.

Council approved the addition of the following members to the Mineral Leather Committee, Messrs. Louis Strymish and F. F. Axelrad.

A letter from Mr. Blair was read and referred to Mr. Kay.

Council approved the rearrangement of names in the Directory by putting all of the mutual members in a separate list.

Council agreed that the Editor should consider the publication of the proceedings of the Wednesday morning practical session. Mr. Williams is to give this consideration and report to Council at the Fall meeting.

Council ordered published in the Journal a letter received from Messrs. Drueding and Faust.

Mr. Teas reported briefly on the meeting finances and advised that the budget established would be followed.

A letter from Mr. S. K. Johnson, in reference to reporting sulfite cellulose when present in an analysis, was referred to Mr. Kay, chairman of the Tannin Analysis Committee.

Council accepted the following new members: Active: Mr. Bertram Christensen, Mr. Otto Eckert, Mr. John V. Geary, Mr. Richard E. Marrs, Mr. Gilbert D. Sart, Mr. Gunars Sultmanis, Mr. Herbert Weinstein.

Transfer to active: Robert C. Purnam.

Associate: Mrs. Edwin S. Cavett; Mr. Henry W. Hansen; Mr. George A. Williams.

Dr. Kirk reported briefly on the plans for 1953 meeting. It was agreed that the Wisconsin Tanners' Production Club should be given a full session for a symposium on leather manufacture. The program is to be left entirely to the Production Club, Mr. W. R. Lotz, President.

Council approved a plan for all publicity to be coordinated through the office of the Secretary. The following committee which represents the Western tanners was approved; Messrs. Lotz, Harry Wilson, F. L. Collins, and Fred O'Flaherty, coordinator.

Council agreed to meet the first week in November, 1952, in Washington, D. C.

The meeting was adjourned.

Respectfully submitted,

FRED O'FLAHERTY, *Secretary.*

ACCEPTANCE OF ALSOP AWARD FOR 1952

By JOSEPH R. KANAGY

Dr. Highberger, Mr. President, members of the American Leather Chemists Association.

I wish to thank the Awards Committee for bestowing on me this recognition which I honor most highly and appreciate most deeply. Such a recognition by you, who understand the work which I am doing, shall always be gratefully remembered.

The contributions, which I have made in the field of leather, are, to a very great extent, the reflection of the efforts of a number of different people, and I would like to take this opportunity to thank them. First of all. . . the National Bureau of Standards, whose facilities for research and consultation are unsurpassed; particularly, I wish to thank Mr. Wallace, Dr. McPherson, and Dr. Kline for providing the facilities for leather research; and my coworkers in the Leather Section and the Division of Organic and Fibrous Materials, who have done much of the laboratory work and have contributed numberless ideas.

Secondly, I wish to thank the Office of the Quartermaster General, which for the past 10 years has generously supported our research work—especially do I thank Dr. S. J. Kennedy, Mr. C. W. Mann, and Dr. Ray Treichler, who have suggested many of our studies and have given valuable advice.

Finally, my many friends in the American Leather Chemists Association, I wish to thank for their timely suggestions on many problems, and for their friendliness.

In behalf of all of these, it gives me great pleasure to accept the Alsop Award for 1952.

Thank you.

The Chemistry of Vegetable Tannins

V. WATTLE

ROBERT C. PUTNAM

United Shoe Machinery Corporation
Research Division
Beverly, Massachusetts

Work on the structure of Black wattle tannin has been reported by several investigators including Corbett,[1] Heugh,[2] Roux,[3] Stephen[6] and Purnam and Gensler[4, 5]. The following products have been reported as having been obtained from the tannin or its methylated derivative by alkaline fusion, permanganate or nitric acid oxidation, and acetylation:

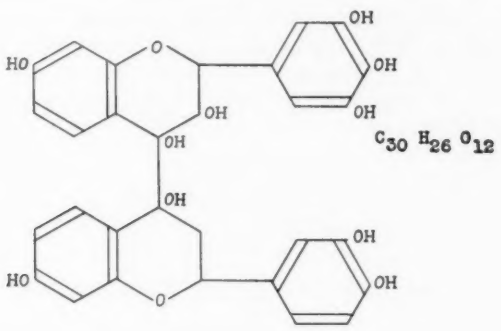
Resorcinol (6), (7)
Gallic acid (6)
Monomethyl resorcinol (2)
Trimethyl gallic acid (1), (2), (6), (9), (11)
Veratric acid (1), (2), (6), (9), (11)
Styphnic acid (6), (8), (9)
3, 5 Dinitro, 2, 4-dihydroxy benzoic acid (10)
5 Nitro, 2, 4-dimethoxy benzoic acid (9)
Dodecacetyl derivative (5)

In order to further clarify the relation between wattle and quebracho tannins, the dodecacetyl derivative of wattle[5] has been deacetylated to a triacetyl derivative. Previously quebracho tannin was shown to yield a triacetyl derivative by deacetylation of its undecacetyl derivative. This would seem to indicate the presence of three aliphatic hydroxyl groups in wattle as well as in quebracho.

A heptamethyl derivative of wattle has been prepared and this may be compared with the heptamethyl compound made from quebracho.

Roux[3] has reported a methylated derivative containing 36.47% methoxyl which corresponds approximately to the expected octamethyl compound that requires 35.9% methoxyl.

If we accept all the experimental evidence recapitulated above as valid including the statement by Roux[3] that terminal methyl groups are absent, a tentative structure may be advanced to explain the data as shown:



$C_{30}H_{26}O_{12}$

It may easily be seen that all of the derivatives and degradation products reported could have been derived from the suggested structure. The formula advanced indicates more than is presently known. The actual position of the bond joining the two halves of the molecule is not known. Likewise the positions of the alicyclic hydroxyl groups have not been determined.

Experimental

The optical rotation of the dodecacetyl derivative of wattle was measured in acetone:

$$\triangle = -0.04 \text{ (0.1 55g. in 13 ml.)}$$

$$\left[\alpha\right]_D^{25°C} = -3.4°$$

Deacetylation

The deacetylation of the dodecacetyl derivative was carried out in the usual manner (4). After ethyl acetate extraction and recovery, it was dissolved in acetone, the insoluble portion removed and the solid recovered from the filtrate, then dissolved in hot water, a further insoluble portion removed and the solid recovered by freeze-drying the filtrate. The product weighed 0.1g. from 1.0g. starting material and had no melting point.

	Calc. $C_{18}H_{22}O_9(OAc)_3$			
	C 61.36	H 4.58	Ac18.33	
Found	C 61.24	H 4.54	Ac18.33	Ash 1.97
	61.09	4.68	18.50	1.63

Methylation

Three grams of purified wattle tannin (5) was suspended in 50 ml. water and methylated with gentle warming by the alternate addition of a solution of 4.5 g sodium hydroxide in 25 ml. water and 10 ml. dimethyl sulfate. After acidification and recovery by filtration it was suspended in 50% methanol,

filtered out and dried in a desiccator. It was then suspended in 25 ml. of absolute ethanol and treated with excess diazomethane in ether. The precipitate was filtered out after 18 hours and washed with ether. It was cream colored and decomposed at 188°C. and was insoluble in boiling 1 *N* sodium hydroxide solution.

	Calc.	$C_{30}H_{18}O_4$	$(OCH_3)_7$	$.H_2O$	
	C 63.97	H 6.10	MeO 31.3	C-Me	None
Found	C 64.07	H 5.96	MeO 31.7	C-Me	None

$\left[\alpha\right]_D^{25°C} = -9.1°$ (0.100 g. in 13 ml. acetone $\Delta = -0.07$)

The rotation was very difficult to read and may not be accurate.

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The Determination of the Over-all Basicity of Chrome Liquors*

By T. C. Thorstensen** and Edwin R. Theis

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In certain of our chrome liquor studies, relative to sugar reduced chrome liquors, it was found that the chromium could not be precipitated free from adsorbed organic matter; in other words, at pH 8.2 (turning point of phenolphthalein indicator) pure chromium hydroxide is not precipitated but a compound of chromium to which is held certain of the sugar degradation products and thus the basicity as determined by the hot titration method (ALCA official method) is in error to this extent. It must be remembered

*Delivered at the Symposia on Chrome Tanning, Wisconsin Tanner's Production Club, 19 January 1952, Milwaukee, Wisconsin.

**Presently with the J. S. Young and Company, Baltimore, Maryland.

that the official method premises the removal and subsequent titration of all the available acids present in the chrome liquor. The calculations for the acidity of a chrome liquor depend on the following equation:

(1) $Cr(OH)SO_4+2NaOH \rightarrow Cr(OH)_3+Na_2SO_4$

going forward to completion.

Feigl and Kraus [1] in 1925 utilized a principle of anion replacement with basic aluminum salts for the analysis of such solutions. These investigators found that a solution of basic aluminum acetate is rendered alkaline when potassium oxalate is added to it. They postulated the following reaction:

(2) $Al(OH)(C_2H_3O_2)_2+3K_2C_2O_4 \rightarrow K_3Al(C_2O_4)_3+2KC_2H_3O_2+KOH$

Blaedel and Panos [2] in 1950 discussed in great detail the several methods for determining the acidity and basicity of aluminum salts. These investigators point out the disadvantages of the potassium fluoride method for determining these factors and show the distinct advantages of potassium oxalate over all other complexing agents. Their method however was for aluminum salts only. The use of the potassium salt was advocated because of its great solubility as compared to the sodium salt.

In the manufacture of "white" chrome tanned leather, oxalic acid is often used along with acid or syntans to give a so-called "bleach" to the grain surface of the chrome tanned leather. The oxalic acid easily penetrates and replaces other anions associated with the chromium and this reaction undoubtedly is the formation of a number of non-tanning reddish purple trioxalato chromiates and thus giving a much less blue color to the grain surface of the skin.

That oxalic acid penetrates and replaces other anions in the chromium complex very easily and almost quantitatively was shown by Theis and Thorstensen [3] in 1946, and by Serfass, Theis and Clark [4] in 1947. These investigators showed by means of spectrophotometric data that if excess oxalic acid were used, that practically all types of complex chromium salts could be easily converted to trioxalato chromiates by the simple expedient of boiling the complex chromium sample with a sufficient excess of oxalic acid. Serfass, Theis, and Clark utilized this principle in developing a rapid colorimetric method for determining chromium in chrome liquors. Modification of this principle to suit conditions should give a measure of the hydroxyl groups removed from the basic chromium salt. The reaction might be written:

(3) $Cr(OH)SO_4+3NaC_2O_4+H_2SO_4 \rightarrow Na_3[Cr(C_2O_4)_3]+1.5Na_2SO_4+0.5H_2SO_4$

Thus it can be stated that the addition of sodium oxalate to a basic chromium sulfate liquor produces a mole of sodium hydroxide for each mole of hydroxyl present in the chromium salt and with the subsequent production of stable sodium trioxalato chromiate. The sodium hydroxide formed is neutralized by the excess sulfuric acid added to the mixture.

Lehigh Method of Determining Over-All Basicity of Chrome Liquors

The method depends upon the removal of the complexed hydroxyl ion with known excess of sulfuric acid and then the formation of a stable chromium oxalate complex after which the entire solution is back titrated with standard base. Since the chromium oxalate complex is not titrated the amount of added acid which is consumed by the reaction is a measure of the hydroxyl groups removed from the complex less the amount of free acid present in the original liquor. In other words, the over-all basicity of the chrome liquor is measured.

Reagents:

1. 2.5 per cent sodium oxalate solution adjusted to pH 8.3 (c. p. $Na_2(COO)_2$)
2. 0.5 *N* H_2SO_4 accurately standardized
3. 0.25 *N* NaOH standardized against the H_2SO_4

Procedure:

A sample of chrome liquor containing between 0.05 – 0.1 gms. Cr_2O_3 is placed in a 250 ml. Erlenmeyer flask. Fifteen ml. of 0.5 *N* H_2SO_4 are added together with 50 ml. of 2.5 per cent sodium oxalate solution. The flask is placed under a reflux condenser, boiled for 1 hour, and then cooled. The contents are transferred to a titrating dish and the cold solution back titrated with 0.25 *N* NaOH to pH 8.3 using a pH meter as an indicator (phenolphthalein may be used but since the endpoint color is masked, the results are not as accurate). A blank containing all the reagents should be run along with the sample.

$$\% \text{ basicity} = \frac{(\text{ml. NaOH blank} \times N \text{ NaOH}) - (\text{ml. NaOH sample} \times N \text{ NaOH}) \times 0.2534 \times 100}{\text{gms. } (Cr_2O_3 \text{ sample})}$$

Notes:

1. The time of boiling under reflux is not critical (1 hour).
2. The limits on chrome concentration in the sample must be adhered to since less than 0.05 gms. Cr_2O_3 does not yield a large enough difference titration for accurate results and more than 0.1 gms. Cr_2O_3 requires both more acid and more oxalate.

Since sugar reduced chrome liquors contain many stabilizing and masking compounds, it seemed fitting to simulate such liquors by studying 33 per cent basic sulfur dioxide chrome liquors to which had been added varying quantities of such stabilizing salts as sodium formate, sodium acetate, and sodium oxalate. Three series of chrome liquors were made, 1) a series containing increasing quantities of sodium acetate up to 6 moles per mole Cr_2O_3, 2) a series similar to (1) but sodium formate used in place of acetate,

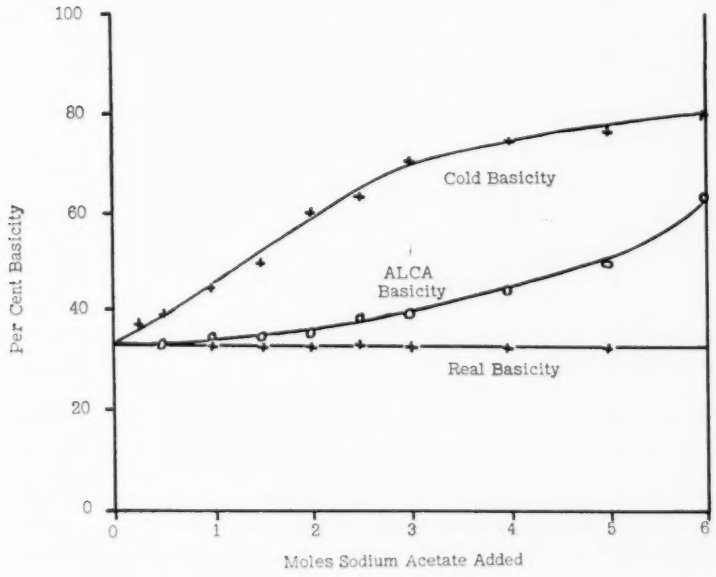
and 3) a series containing sodium oxalate up to 3 moles per mole of Cr_2O_3. All of these liquors were made up cold and allowed to age for one week. After ageing, each solution was analyzed for Cr_2O_3. The basicity of the various solutions was obtained by 3 methods, 1) the cold method or a rapid titration cold to pH 8.2, 2) the hot method (ALCA) or a rapid titration hot to pH 8.2, and 3) the Lehigh method as described earlier in this report.

The Effect of Sodium Acetate, Formate, and Oxalate on Basicity

The addition of such salts as sodium acetate, formate, or oxalate to the 33 per cent basic chrome liquor should not materially change the over-all basicity figure of the liquor. True, there will be coordination, little to great, of certain of their anions with the chromium. In the determination of over-all liquor basicity by the hot titration (ALCA) method, true values are obtained only if the complexly associated anions can be replaced by hydroxyl ions at pH 8.2 at 100°C. For the case of "sulfato" groups, this replacement is almost

Figure 1

EFFECT OF SODIUM ACETATE ADDITIONS TO A SULFUR DIOXIDE REDUCED CHROME LIQUOR UPON BASICITY

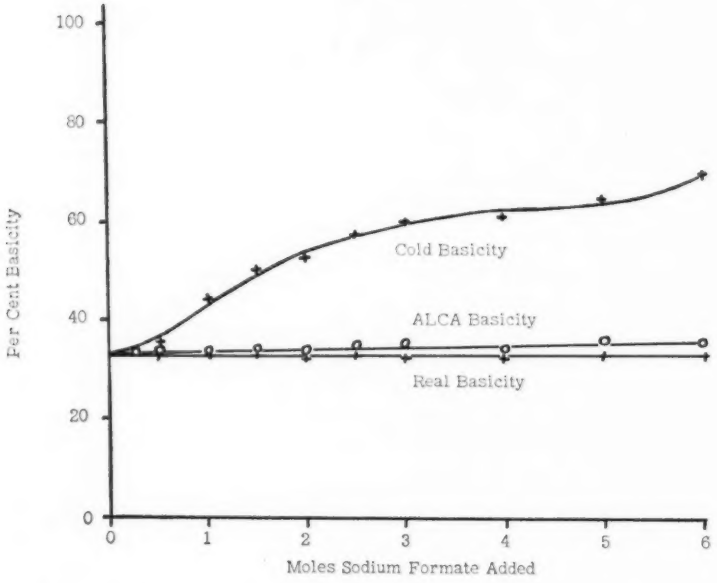


quantitative in character but for strongly held organic anions, complete displacement generally does not obtain and thus errors are evident. In contradiction to the hot titration method, the cold basicity method, if carried out rapidly, causes only slight displacement of complexly held anions, therefore the cold titration data are usually high.

The addition of sodium acetate to a basic chromium sulfate solution brings about both masking and stabilizing of the basic chromium salt and therefore data obtained by the hot titration method are in some error. Data, obtained from the sodium acetate series, are shown in Figure 1. As can be seen by a study of the data, the curve representing the Lehigh method shows no significant error over the range investigated, whereas, the curve for the hot titration method indicates a constant increasing error with increasing amounts of added sodium acetate.

Figure 2

EFFECT OF SODIUM FORMATE ADDITIONS TO A SULFUR DIOXIDE REDUCED CHROME LIQUOR UPON BASICITY



Sodium formate additions stabilize the basic chromium salt to pH values approximately 6.0 but not to the higher pH values obtaining for acetate

additions. It takes large quantities of formate anions to bring about real and stable association (in the cold) with the chromium. A study of Figure 2 shows that the hot basicity (ALCA) and the Lehigh method give for all intents and purposes the same results with the Lehigh method giving the lower values as should be the case.

Figure 3

EFFECT OF SODIUM OXALATE ADDITIONS TO A SULFUR DIOXIDE REDUCED CHROME LIQUOR UPON BASICITY

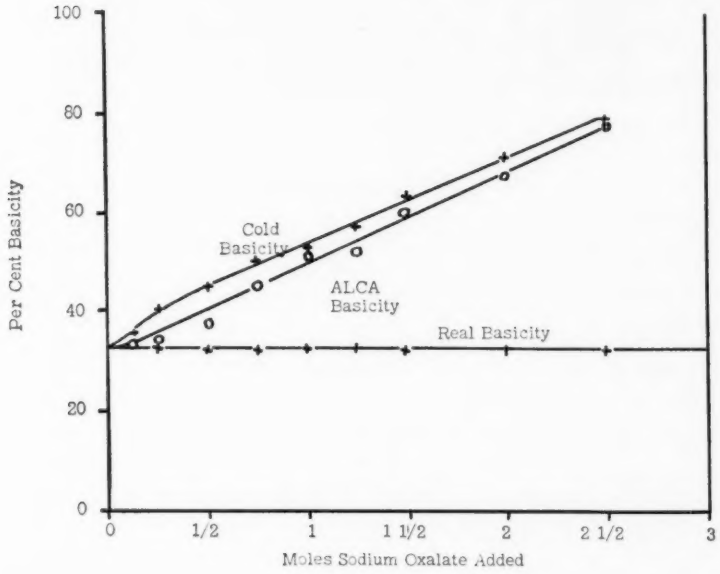


Figure 3 shows the effect of sodium oxalate additions. In this case, the oxalate associates very readily with the chromium and gives an extremely stable complex even into the high pH ranges and therefore the basicity values obtained by the hot titration method should be decidedly greater than those by the Lehigh method—such is the case. For oxalate additions, the cold and hot titration methods give almost the same values indicative of a very stable complex.

The method outlined in this report has been used with a number of *normal* sugar and sulfur dioxide reduced chrome liquors and has given excellent

results. The authors believe that it will yield more nearly true basicity values than any of the previous methods proposed for determining this factor.

ACKNOWLEDGMENT

The writers take great pleasure in expressing their appreciation for the financial support and encouragement of the studies reported herein by the American Cyanamid Company, the Mutual Chemical Company of America and the Diamond Alkali Company.

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Received March 7, 1952

Brazilian Tannins

By E. BELAVSKY and E. TERMIGNONI

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Guapore, R. G. S. Brazil

Brazil has numerous resources in all three kingdoms, animal, mineral and vegetable, still undeveloped or even investigated. Vegetation, favored by surplus rainfall and a benign tropical sun, flourishes luxuriantly. Only such exceptional conditions could create the enormous forests of the Amazon region, in northern Brazil and in Mato Grosso, as well as the ever increasing number of plantations of species rich in tannins in the southern states. For example the Acacia Negra plantations in the Rio Grande do Sul, started only twenty years ago, have reached an area of seventy million square feet.

We have seen high, thickly wooded eucalyptus forests not yet six years old, alleys of lovely three year old mimosa (Acacia Negra) and bamboo. Vegetable tannins, like everything else here in Brazil, have been little studied or developed and await future pioneers. In all probability those pioneers will find a number of other vegetable tannins besides those already used in this country. People here use several kinds of home made tannins for the purpose of making leather. Their fathers and grandfathers have produced good leather with them. Often bark, containing 15-20 per cent tannins is used, while wood containing an equal percentage of tannins, is burned.

In this article we should like to discuss only those tannins in general use for making leather.

FIGURE 1—Plantation of Barbatimao Batatuba, Sao Paulo

Quebracho.

First of all consider quebracho wood—Quebracho Colorado (Quebrachia Lorentzii, Gris.). Quebracho is not only used for the purpose of making tannin extracts, but it is also valuable for other purposes on account of its hardness and firmness. (The name quebracho means: quebra acha—breaks the hatchet). In Brazil it grows mostly in Mato Grosso. Near the Parana River there are tanning extract plants, some of which are quite modern.

There are three different kinds of quebracho trees: 1. Urundai' 2. Colorado. 3. Quebracho Femea.

For extraction purposes, trees 100 or 200 years old, 15 to 20 meters high and weighing about 1000 kilos are required.

Generally the quebracho trees grow deep in the jungle and during the dry season are transported to a river or railway station on special carts pulled by six or eight oxen. The first operation of a tanning extract plant is the preparation of chips by means of special heavy machines (chippers) due to the hardness of the wood. The modern factories have 8 or 12 extractors made of copper and arranged for continuous counter current extraction under pressure (1.5–2 atm.) and 120–130 degrees centigrade. From the extractors, liquors with about 7 per cent tannins are obtained and afterwards are evaporated in a regular triple effect vacuum evaporator concentrating to 35 to 50 per cent tannins. The liquid extract is then pumped into a vacuum evaporator equipment of special construction, where it is left for 16 or 18 hours until it reaches the desired density. When it becomes dense like resin, the black extract with a reddish shade is placed in double sacks (48–50 kgs.) which are left for 48 hours until the extract is quite hardened. This hardened ex-

FIGURE 2—Plantation of Barbatimao Batatuba, Sao Paulo

tract may now be stored. Before shipping, the extract must lie in storage at least 120 hours. This extract contains 62–63 per cent tannins, 7–8 per cent non tannins, 7–8 per cent insolubles, 20–23 per cent water. Fifty hours is required to accomplish production. The extracted chips, containing about 40 per cent of water, are used for heating and other purposes.

Barbatimao

The most used and best Brazilian extract is produced from the bark Barbatimao (Barba de Timon – Stryphnodendron Barbatimon Mart. In Portuguese is called Cortex Astringens Brasiliensis). The exploitation of young Barbatimao forests is already on an industrial scale. Every three years in autumn, the cutting takes place. One "alqueire" (2–4–ha.) produces about 100 "arrobas" (1 arroba - 15 kilos) of dry bark. The bark is gray-brownish, the cut reddish-brown, has an average thickness of ½ cm.

A smooth bark contains:

	Average Per cent
Tannins	27
Non-Tannins	4
Insolubles	54.5
Water	14.5
Sugar	1.1

In January it blooms and has fruit in March.

The liquor produced from this bark tans quickly and gives a good yield. The color of the leather is reddish, but without bleaching is rather dark.

FIGURE 3—Branch of Acacia Negra

The fruit shells contain about 27 per cent tannins, the wood about 14 per cent. However, generally they are not used for leather tanning.

Angico.

Piptadenia rigica Benth.

This is the name of many mimosa trees, but in different parts of the country nomenclature varies. Angico is found from Maranhao down to Rio Grande do Sul. The bark is used for leather producing purposes and sometimes also the wood is used for tanning. The extract is produced in the state of Paraiba only. In general the Angico tree is divided into two groups: the white and the red. They contain the same quantity of tannins.

Angico de Campo	Per cent	*Angico de Mato*	Per cent
Tannins	20.1	Tannins	16.0
Non-Tannins	5.9	Non-Tannins	9.5
Insolubles	59.5	Insolubles	60.0
Water	14.5	Water	14.5
Sugar	2.0	Sugar	1.0

FIGURE 4—Plantation of six year old Ac. Negra—Rio Grande do Sul Guapore

Acacia Negra.

Acacia Decurrens, Wild, molissima, is cultivated in the state of Sao Paulo and mostly in the southern states of Rio Grande do Sul and Santa Catarina. The bark contains its largest quantity of tannins when the tree is between three to four years old, as is shown in the following table:

Years	Per cent Total Solids	Per cent Non Tannins	Per cent Tannins
4	44.9	8.8	36.1
6	38.7	10.7	28.0
8	39.6	7.6	32.0
12	40.5	7.9	32.6

FIGURE 5—Plantation of eight year old Ac. Negra—Guapore Rio Grande do Sul

A sample of Rio Grande do Sul's Acacia bark gave the following analysis:

	Per cent
Tannins	41.4
Non Tannins	10.6
Insolubles	33.5
Water	14.5

In the experimental felling of 5 years old Acacias made by us, one tree gave 8–10 kilos of dry bark and 0.25 cubic meter of wood. Trees sixty years old reached in diameter: 50 per cent - 6 inches; 30 per cent - 7 inches; 10 per cent - 8 inches.

FIGURE 6—Felled trees Acacia Negra Guapore, Rio Grande do Sul

Average analyses of the extracts prepared from the bark are:

Liquid Extract: Specific Gravity - 1.325 (20 degrees C.)

	Per cent
Water	40.0
Tannins	42.1
Non Tannins	17.4
Insolubles	0.5
Sugar	8.2
Solid Extract:	
Water	21.1
Tannins	54.5
Non Tannins	22.4
Insolubles	2.0
Sugar	8.9
Dry Powdered Extract:	
Water	8.8
Tannins	66.2
Non Tannins	22.5
Insolubles	1.5
Sugar	9.2

FIGURE 7—The drying of bark

Mangue.

Mangua trees belong to different botanic groups: Rhizophora (Rhizophoracees) Avicennia (verbacees) Laguncularia (Combretacees) Cassipouera (Rhizophoracees) and grow chiefly in the Atlantic Ocean Coast region from Para to Rio Grande do Sul, on valleys near rivers and banks of lakes (Amazonas). Their leaves and branches renew rapidly so that they form thick forests "Manguesaes". For leather production purposes the leaves and bark are employed. For instance, the tanneries of Santos, Sao Paulo and its environs consume about 1,800 cubic meters of bark and 1,350,000 kilos of leaves during a year. The tanneries in Santa Catarina get their tannins almost exclusively from leaves of mangue trees and have a yearly consumption of 400,000 kilos.

Dry Leaves contain:

	Per cent
Tannins	20.0
Non Tannins	16.0
Insolubles	49.5
Water	14.5
Sugar	4.2
Bark from Candapauva:	
Solubles solids	32.1
Non Tannins	17.3
Tannins	14.8

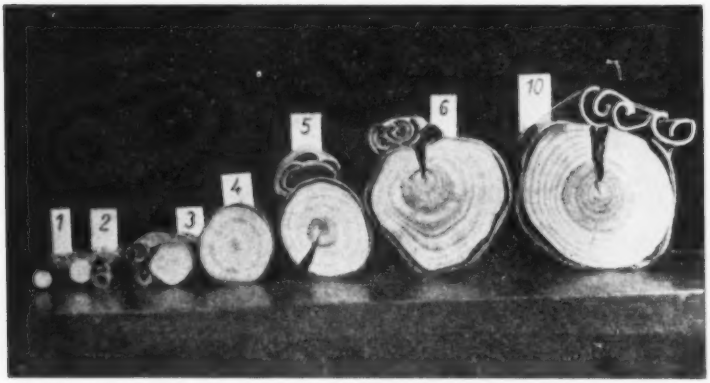

FIGURE 8—The increase in diameter of the tree with age 1–10 years

Winter (July–September) is the best time for harvesting. From 100 kilos of leaves 16–20 kilos of 40Be′ extract are obtained. Fresh leaves have about 70 per cent water, 5–10 per cent tannins; 1000 kilos of leaves producing 1000 kilos of 7–8 Be′ liquor.

The trouble with mangue trees tannins is that they contain a large amount of sugar. On 100 parts of tannins in fresh leaves, there are about 80–85 parts; in evaporated extract there are 128–156 parts and in powder extract 158 parts. During the preparation of extract the non tannins increase. The extract in powdered form contains:

	Per cent
Tannins	37.3
Non Tannins	59.0
Insolubles	1.0
Water	2.7

Also, the leaves contain a large quantity of ash and that is the reason why the liquid extract has about 10 per cent ash and the solid powder up to 16 per cent. pH of the solution is 4.5 – 4.5.

This extract is successfully used in local tanneries for coloring and filling chrome leather, replacing Gambier and Sumac.

In the following table is shown the content of tannins in different Brazilian plants.

Name	Botanic Classification	Part of Plant	Per cent Total Solids	Per cent Non Tannins	Per cent Tannins
Barbatimao	Stryphnodendron barbatimao	Bark	30.9	8.3	22.6
Angico	Piptodenia rigida	Bark	25.5	10.5	15.0
Acacia Negra	Acacia decurrens	Bark	40.9	8.7	32.3
Apertaruao	Piper aduncum	Leaves	17.5	8.1	9.4
Capororoca	Rapanea ferruginea	Bark	19.3	8.5	10.8
Goiabeira	Psidium guaiava	Bark	25.4	9.9	15.5
Jatoba	Hymenoea stilbocarpa	Bark	33.6	14.5	19.1
Mangue Vermelho	Rhizophora mangue	Bark	32.1	17.3	14.8
Murici	Byrsonima verbascifolia	Bark	27.7	7.4	20.3
Sibipiruna	Caesalpinia tinctoria	Wood	22.1	7.3	14.8

SUMMARY:

The enormous sources of tannins in Brazil are indicated by the analyses of many plants and the extracts produced from them.

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The Mechanism of Vegetable Tannage

By S. G. SHUTTLEWORTH

INTRODUCTORY

In an extensive review, the writer and Dr. Cunningham [1] have examined the literature on vegetable tanning and have concluded that the various phenomena of vegetable tanning can be explained adequately on the hydrogen bond theory, each tannin molecule and each protein chain being capable of multi point hydrogen bond attachment. Since the publication of this paper,

Lollar and his co-workers [2, 3] have produced further proof that the salt forming function of the free amino group of the hide substance is a relatively insignificant factor in the case of the natural tannins, while Tu and Lollar [4] have carried out an examination of the tanning properties of a number of phenolic substances, from which they have concluded that tanning is due to hydrogen bonding which probably occurs at the peptide linkage of the collagen. They have found that *ortho*- and *para*-hydroxy compounds tan better than *meta*- compounds, confirming our earlier suggestion that greater resonance would be likely to give stronger hydrogen bonds. The structure of collagen has also received further attention, and the model proposed by Pauling and Corey [5] enables a clearer picture to be formed of the stereochemical aspects of tanning.

Some General Theoretical Considerations

A common feature of all vegetable and synthetic tannins is that they are organic compounds of large molecular weight which would normally be completely insoluble in water except for the presence of strongly lyophilic groups. This implies the recognition of two oppositely acting forces. One of these is the tendency for the water molecules to thrust the lyophobic parts of the molecule out of solution, while the other is for the lyophilic parts of the molecule to draw the molecule into solution. If these lyophilic parts of the molecule are attracted to or held by receptive sites on a third component in the system, the equilibrium will be moved towards reduced solubility. The solvent need not be water, and the system is an equilibrium which will be influenced by the relative concentrations of solute and the third component in the solvent. Provided that the reaction between solute and the third component is also reversible, it is logical to expect the Langmuir and Freundlich adsorption equations to be followed, without in any way proving anything about the nature of the forces involved between the solute and the third component. It is thus apparent that the description of tanning as "adsorption", "sorption" or "polar adsorption" and the plotting of Langmuir and Freundlich adsorption curves [6], is a recognition of the reversible competition between water and protein for the tannin, without proving anything about the nature of the forces involved. The "polar adsorptionists" [7] have shown that these forces are also linked with polarity and surface tension.

There are three forces which have in the past been invoked to explain the mechanism of vegetable tanning:-

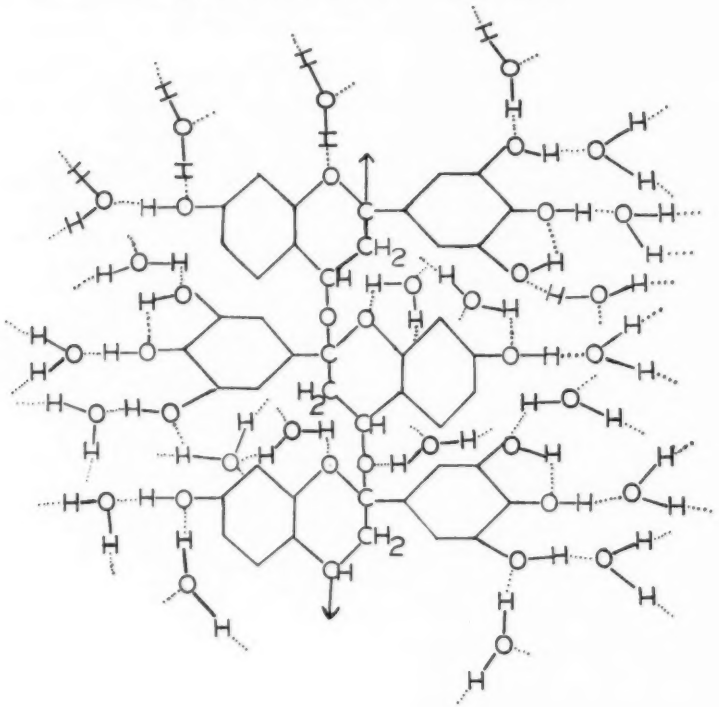
(a) *Electrovalent Forces.* These imply the existence of positively or negatively charged ions of the kind responsible for the lyophilic properties of cationic and anionic detergents and wetting agents. Consider, for example, a sulphonic acid group with a large paraffin chain attached. On contact with water, the highly mobile positively charged hydrogen ions become distributed through the water and the potential difference thus created draws into solu-

tion the negatively charged strongly lyophilic sulphonic acid groups together with their lyophilic paraffin chains. A similar mechanism operates for the soluble salts of the sulphonic acid group. It is important to note that these forces disappear if ionisation ceases, and that a soap loses its solubility as soon as it is converted from the sodium salt to the carboxylic acid form. Thus, at the normal pH of tannage (pH 3.0 – 4.0), the operation of an electrovalent mechanism is likely to be confined to strong acids. At this pH range the lyophobic nature of the un-ionised carboxy groups is considered to be due to hydrogen bond forces, each hydrogen bond being able to hold a limited amount of lyophilic chain in solution, as evidenced by the limited solubility of butyric, benzoic and phthalic acids at low pH values. The mechanism of solubility differs greatly, as the molecule is no longer in two electrovalent parts, one of which is freely dispersed and hence drawing its oppositely charged partner into solution. The molecule is now a single unit attached to water molecules by hydrogen bonds.

(b) *Hydrogen Bonds.* The mechanism of hydrogen bonds has received full consideration in our earlier paper. A simple static picture of this bond follows from the recognition of the geometric fact that a positive charge distributed over the surface of the hydrogen atom is unable to neutralize adequately the negative charges distributed over the surfaces of very much larger atoms, particularly if the increase in surface is vastly out of proportion with the additional number of charges carried, as in fluorine (one charge), oxygen (two charges), and nitrogen (three charges). The result is that the hydrogen will carry a small residual positive charge, while its associated atom will carry a small residual negative charge, both of which may be enhanced by resonance effects. Thus the average polar solvent such as water has structural characteristics due to hydrogen bends, and will tend to draw into solution compounds capable of donating and receiving hydrogen bonds. Fig. 1 shows a two dimensional picture of an approximate structure of a wattle tannin molecule in aqueous medium. It is apparent that the multiple hydrogen bond sites of the tannin cause it to become surrounded by an envelope of hydrogen bonded water molecules, thus accounting for the complete miscibility of so large a molecule with water.

(c) *Adsorption Forces.* These are due to weak residual charges of a much lower order of strength than the hydrogen bond, and therefore of negligible consequences in any system lavishly endowed with hydrogen bonds. However in the case of certain types of synthetic tannin, where a large lyophobic molecule is held in solution by comparatively few lyophilic groups, the tendency of the lyophobic part to be held by weak residual charges to a compatible third component may well be sufficient to remove it from solution. If the third component is a protein, it seems most unlikely that these adsorptive forces will compete successfully with the hydrogen bonded water of the

FIG. 1. APPROXIMATE STRUCTURE OF AQEOUS WATTLE TANNIN.

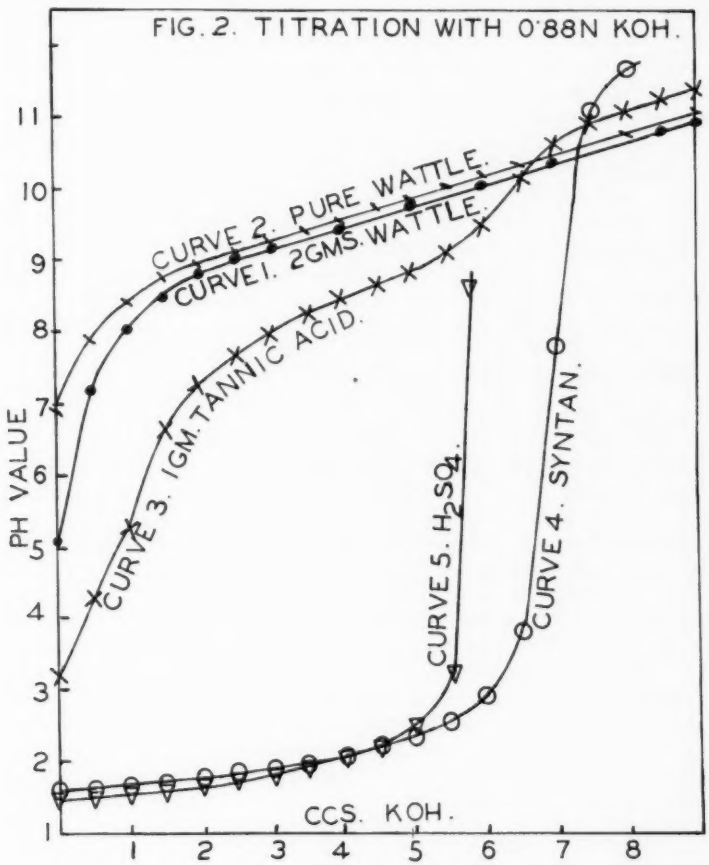


protein, so that the compatible sites will most probably be confined to the non polar parts of the side chains.

pH Titration Curves

In order to bring out the differences in tanning mechanism caused by the operation of the three types of bonding force discussed above, the experimental work has mainly been devoted to a comparison between wattle tannin and a naphthalene sulphonic acid syntan, the former to illustrate a purely hydrogen bond mechanism, and the latter the electrovalent and adsorptive mechanisms.

Fig. 2 shows the titration curves of these two materials and also of tannic acid.



(a) *Wattle Tannin.* Curve 1 gives the titration of a sample of commercial wattle extract in which is present a small percentage of non tanning organic acids, (acetic, gallic, etc.). These acids can be eliminated by appropriate methods of purification, resulting in curve 2, from which it is apparent that wattle tannin commences titrating above pH 7.0, and gives a continuous line due to the titration of numerous aromatic hydroxy groups of overlapping pK values. Roux[8] has shown that wattle tannin has one fully active pyrogallol unit per C_{18}, which therefore gives an equivalent weight of approximately 290 for the most acidic hydroxy group in the unit, which from curve 1 corres-

ponds to a pK value of 9.25. Calculation shows that an aqueous solution of wattle tannin at pH 3.0 will contain less than one ionised group per million C_{18} units or per four million OH groups. This proves that electrovalent forces are of negligible consequences at this pH value. The suggestion of the salt formation theorists is that wattle tannin can be fixed by progressive precipitation due to interaction between this rare charged molecule and a charged protein amino group, although the combining power of collagen for wattle tannin would imply the neutralization by each amino group of a wattle tannin molecule of at least the size of that illustrated in Fig. 1. In other words, it is a prerequisite of the salt formation theory that the neutralization of the lyophilic attraction of only one of the pyrogallol OH groups of Fig. 1 is sufficient to change the molecule from complete miscilility to extremely low solubility, in spite of the evident fact that the aqueous envelope will scarcely be disturbed, as more than 95% of the lyophilic groups responsible for solution of the molecule are not affected.

(b) *Tannic Acid.* Curve 3 of Fig. 2 shows the titration of B.D.H. Tannic Acid. It is evident that there is a carboxyl group of pK value approximately 4.7 giving an equivalent weight of approximately 750, plus acidic hydroxy groups of average pK 8.5 at least three times as abundant as the carboxyl group, and further acidic hydroxy groups titrating above pH 10.5. Calculation shows that, at pH 3.0 and normal tanning concentrations, about one carboxyl group in every 60 will be ionised, i. e. one per 45,000 molecular weight, which is not likely to be an appreciable contributor to the solubility mechanism of tannic acid. However, the molecule of tannic acid is lavishly endowed with groups capable of hydrogen bonding with water, so that the solubility mechanism is suggested to be similar to that of wattle. The contribution of electrovalent forces to the combination between tannic acid and collagen, though much greater than that of wattle tannin, is likely to be negligible at pH 3.0, though appreciable between pH 4.0 and the isoelectric point of the protein. At higher pH values the protein will be negatively charged and this will tend to repel the ionised tannin.

(c) *Naphthalene Sulphonic Acid Syntan.* Curve 4 shows the titration curve of a naphthalene sulphonic acid syntan, while curve 5 shows the titration of sulphuric acid. It is evident that the acidic groups are fully ionised through most of the pH range. The absence of hydrogen bond forming groups in the non ionic parts of the molecule makes it possible to conclude that solubility and tanning will be due to electrovalent and absorptive forces.

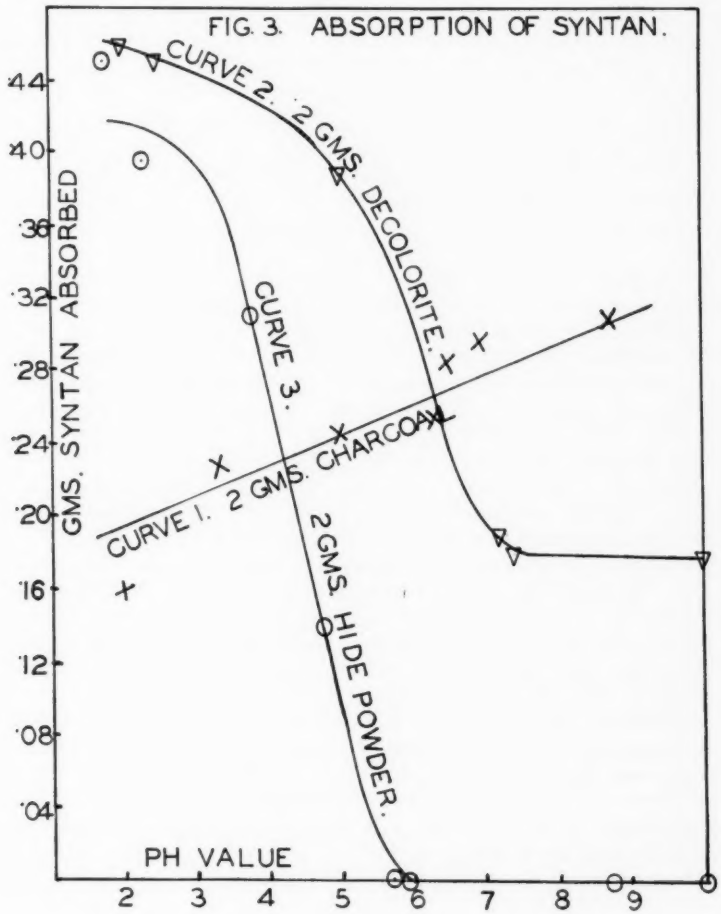
Fixation of Naphthalene Sulphonic Acid Syntan

Fig. 3 shows the uptake from aqueous solution of a naphthalene sulphonic acid syntan by various materials at different pH values. These materials were as follows:-

Hide Powder. Approved by I.S.L.T.C. Committee for tannin analyses, Batch No. c, 11.

Decolorite. An acid exchange resin supplied by the Permutit Co. and stated to contain amino groups and large pore spaces suited to large molecules. In order to prevent the collapse of these pore spaces, the resin was maintained in a wet condition between manufacture and use.

Wofatit C. A base exchange resin stated by the makers to contain both carboxy and aromatic hydroxy groups.



Wofatit KS. A base exchange resin stated by the makers to contain both sulphonic and aromatic hydroxy groups.

Structures for Wofatit C and KS are given in B.I.O.S., Report No. 621.

Charcoal. B.D.H. activated charcoal for decolorizing.

Cellulose. Standard Solka-Floc, a wood cellulose of 99.5% purity. Very finely divided.

In all cases adsorption took place from 1% solutions of syntan, not more than one fifth of the syntan being removed from solution at equilibrium. The solutions were maintained in contact with the adsorbing material with periodic shaking for a week at room temperature, this having been determined as adequate for equilibrium.

No appreciable fixation of the syntan at any pH could be detected with Wofatit C, Wofatit KS, and Cellulose.

Curve 1 of Fig. 3 shows that the uptake of syntan by charcoal exhibited a marked increase with increasing pH value, but there appeared to be no obvious correlation with the syntan titration curve, although the lack of correlation may have been due to the difference between internal and external pH due to adsorbed syntan. It would appear that the acidic form of the syntan gives the charcoal a high surface charge which inhibits further adsorption. Neutralization of syntan appears to overcome this, possibly due to adsorption of sodium ions which are less mobile than hydrogen ions.

Curve 2 of Fig. 3 shows the uptake of syntan by Decolorite. It is apparent that the effect is a dual one, being partly electrostatic attraction, which operates below pH 7.0, and partly adsorption, which is relatively independent of pH, and is responsible both for the residual fixation of syntan above pH 7.0 and the pronounced shift of the curve from a lower pH region which would be the normal strong acid titration curve of Decolorite.

Curve 3 of Fig. 3 shows the hide powder uptake curve, which, by comparison with curves 1 and 2 would appear to be entirely an electrovalent reaction, as no syntan uptake above pH 5.5 was detected.

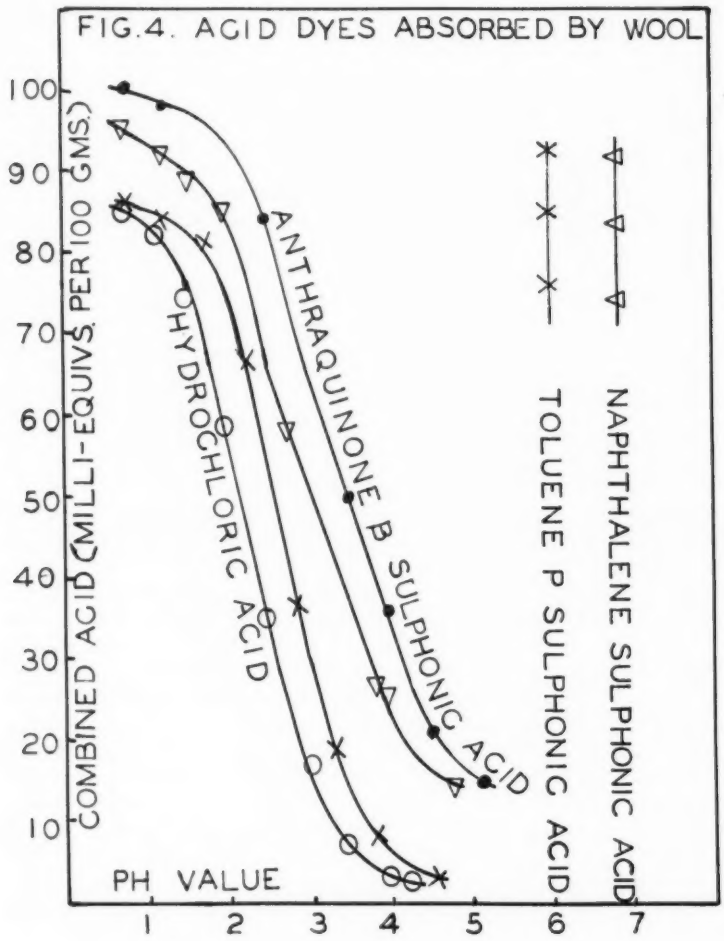
In view of the "Salt formation" theory of tanning, it seems important to explore the significance of curve 3 of Fig. 3 in some detail. At the lowest pH value excess ionised syntan is in equilibrium with hide powder. Hydrogen ions are absorbed to back titrate the protein side chains, giving positive charges to all the basic groups. The loss of hydrogen ions from the solvent without an equivalent loss of anions would leave an excess of negative ions in the solvent phase, so that the syntan ions follow the hydrogen ions into the protein and occupy positions adjacent to the positively charged amino groups, thereby reducing the free energy of the system to a minimum. This means a stoichiometric relationship between basic groups of the protein and syntan uptake at the lowest pH value. If, however, the syntan was a weak acid, and the low pH value was produced by the addition of a mineral acid, the latter would supply the hydrogen ions to the protein, and the attraction of the

positively charged protein would be shared between the mineral acid anion and the very low proportion of ionised weak acid groups. If these groups were freely soluble as in natural tannins, there would seem to be no reason to expect their fixation by protein in preference to the far more abundant charged mineral acid anions. At the isoelectric point the charge on the protein is zero, so that it is logical to expect the uptake of charged anions held by electrovalent groups to be zero. Any syntan fixed at the isoelectric point is thus a measure of the syntan held by adsorptive or other forces. As Peters [9] has pointed out, if a hydrocarbon nucleus is repelled by water molecules in solution, there will be a decrease in free energy due to deposition of the hydrocarbon on any available non polar sites, even without assuming attractive forces between the absorbing medium and the hydrocarbon part of the solute molecules. As further alkali is added to raise the pH value above the isoelectric point, the protein becomes increasingly negatively charged by taking up alkali added to raise the pH. If the syntan is a strong acid, it will remain as the fully ionised sodium salt, and its anion will be repelled by the protein. If it is a weak acid, more alkali will be needed to titrate the acid to its sodium salt in order to raise the pH to the desired level. The negatively charged protein will repel the negatively charged syntan anion.

The parallel problem of the uptake of acid dyestuffs has received extensive attention in Textile Chemistry. Fig. 4 shows curves given by Speakman and Elliott [10] for acid combining capacity of wool which demonstrate the same phenomena as that observed for the combination of naphthalene sulphonic acid syntan with hide powder (curve 3 of Fig. 3). They have confirmed the work of many others that, when expressed in milli-equivalents, the uptake from solution of these sulphonic acid compounds can be expressed stoichiometrically in terms of the combining power of the amino groups of the protein, regardless of whether the dyestuff molecule is mono, di or tri valent. Further, that if the amino groups are only partly saturated with dyestuff, the amount of acid then taken up is proportional to the calculated amount of unreacted amino groups. Miekeley [11] has shown that the acid binding capacity of collagen is not seriously impaired by tanning with natural vegetable tannins.

Calculation of the number of milli-equivalents of syntan absorbed by hide powder from curve 3 Fig. 3, gives a figure of 101 milli-equivalents per 100 gms. of hide powder, compared with the acid combining figure of 85 given by McLaughlin and Theis [12]. In the case of wool dyeing, Speakman and Elliott (loc. cit.) attribute their somewhat high result to (a) slight decomposition of peptide groups under very acid conditions, (b) aggregation of solute molecules, and (c) adsorption of undissociated molecules.

An important general observation which deserves consideration is the tendency for naphthalene sulphonic acid syntans and polyvalent ions such as phosphate to restrict swelling. Speakman and Elliott have shown that the

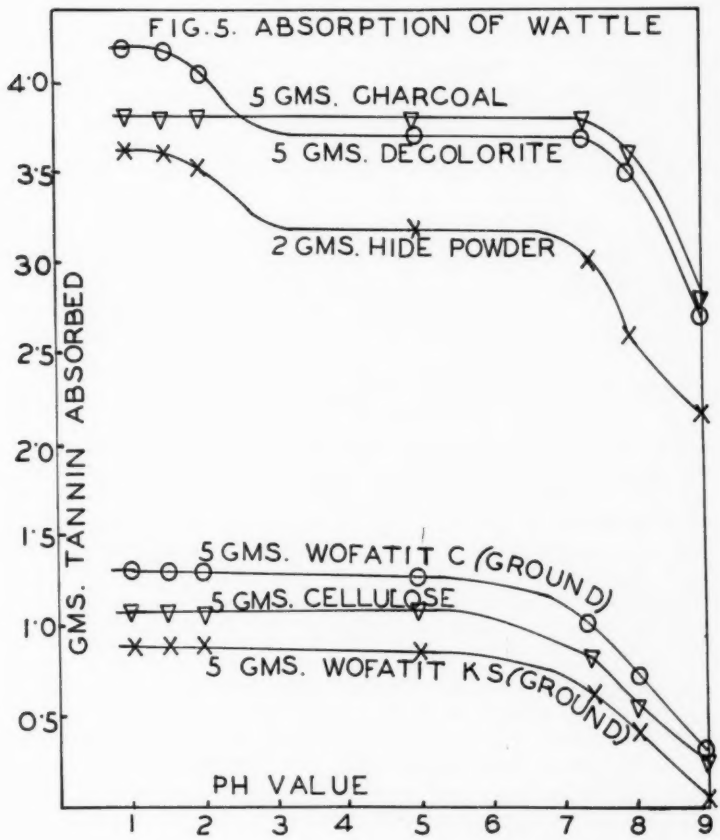


combining power of phenol 2–4–6 trisulphonic acid for wool is such that all three negative groups are able to combine stoichiometrically with all the amino groups present, in spite of the fact that it is stereochemically impossible for all the sulphonic acid groups to occupy adjacent positions to their oppositely charged counterparts. The potential differences set up will be minimized by electron mobility, but are still likely to have a powerful restraining effect

on the swelling. Thus it does not seem necessary to invoke the idea of the anion bridge to explain reduced swelling by multivalent strong acids.

Fixation of Wattle Tannin

Fig. 5 shows the equilibrium uptake of wattle tannin at room temperature by various adsorbents at various pH values. Compared with the reactivity of the syntan, it is apparent that the ability of wattle tannin to hydrogen bond has given it a far wider affinity for adsorbent than that conferred by the electrovalent activity of the syntan. A second remarkable point is the similarity in form of all the curves between pH 3.0 and 9.0, a common factor



being the profound fall in uptake at pH values above 7.0. Reference to the titration curve for wattle tannin (Fig. 2) shows that this is the pH range where the hydroxy groups are titrating, thereby substituting electrovalent forces for hydrogen bonds in the solubility mechanism. The alkali added to the system to raise the pH above 7.0 is shared between the adsorbent and the tannin. This changes the tannin molecules from self contained units surrounded by envelopes of hydrogen bonded water molecules, to negatively charged anions plus an equal number of positively charged cations. The latter are not attracted to the adsorbent because it is already in equilibrium with alkali, so that an electrostatic attraction is set up between external cations and internal ionised tannin in proportion to the relative number of charged and uncharged tannin molecules.

A second point which arises from these curves is that the sulphonic acid resin Wofatit KS and the carboxy resin Wofatit C both show marked affinity for wattle tannin. However the absence of a comparatively marked increase in affinity of the carboxy resin in changing from pH 5.0 to 3.0, suggests that the carboxy group is not playing a major role in tan fixation, even though capable of hydrogen bonding at low pH values. The affinity of cellulose for wattle tannin is also worthy of note.

Unfortunately the accessibility factor prevents undue emphasis being placed on the relative amounts of tannin absorbed. This is illustrated by the fact that an amino resin Wofatit M, ground similarly to the Wofatits C and KS used in Fig. 5, gave about the same order of tan uptake, compared with the much higher uptake of Decolorite which had pore spaces giving access to the molecular network.

It seems very significant that the only materials which showed considerable increases in tan uptake in changing from pH 5 to pH 1 were those which possessed channels giving access to the molecular network, viz., hide powder and Decolorite, and in order to ascertain whether this increased tannin absorption was due to swelling at lower pH values, two intrinsically different controlling factors were introduced. The obvious one was to repress the swelling by the addition of salt, but in view of the swamping effect of salt on other possible effects, it was also decided to use the tannin itself to control the swelling, by adjusting the pH only after an initial 2 day tannage at pH 4.8, followed by tanning to equilibrium at the new pH. The results are given in Tables 1 and 2.

The somewhat higher values of the salt treated extract, may have been due to salting out, as tannin absorption was measured by difference. In the case of the pretanned hide powder, the pretannage was at a 25% higher concentration in order to permit the addition, after 48 hours, of 25 ccs of water containing 0, 5 and 20 ccs of $\frac{N}{2}$ HCL. It is evident that this has given a

TABLE I

pH Effect on Decolorite Uptake of Wattle Tannin
(Gms. Tannin absorbed by 5 gms Decolorite)

pH Value	Normal Tannage	Tanned in the presence of 5% NaCl	Pretanned at pH 4.8
4.8	3.70	3.80	3.80
2.0	4.05	3.79	3.80
1.0	4.19	3.76	3.84

TABLE 2

pH Effect on Hide powder Uptake of Wattle Tannin
(Gms Tannin absorbed by 2 gms Hide Powder)

pH Value	Normal Tannage	Tanned in the presence of 5% NaCl	Pretanned at pH 4.8
4.8	3.20	3.33	3.33
2.0	3.53	3.27	3.27
1.0	3.62	3.27	3.39

somewhat higher fixation, which has not been reversed completely after a further 4 days tannage under the more dilute conditions.

The results prove that the increased tannin uptake at lower pH values is due to swelling, which increases the accessibility of the protein or resin to the tannin. A second result, which is of considerable practical significance, is that the set of the fibre structure and the ultimate tan uptake are both to a very large extent dependent on the early stages of tanning, and independent of the later stages.

The use of typical Langmuir curves to characterize the concentration effect on tan uptake by various materials is shown in Fig. 6. The fact, that the points lie on straight lines merely indicates that a reversible reaction is involved, as illustrated by the dotted line which has been calculated for the ionisation of a simple menobasic acid.

Stereochemical Considerations

The importance of accessibility as a factor in tanning has been emphasized in the above experiments. The latest stereochemical model of collagen to be published is that of Pauling and Corey [5] who visualize the collagen molecule as consisting of three helical polypeptide chains hydrogen bonded together by their – N – C – groups.

FIG. 6. LANGMUIR CURVES.

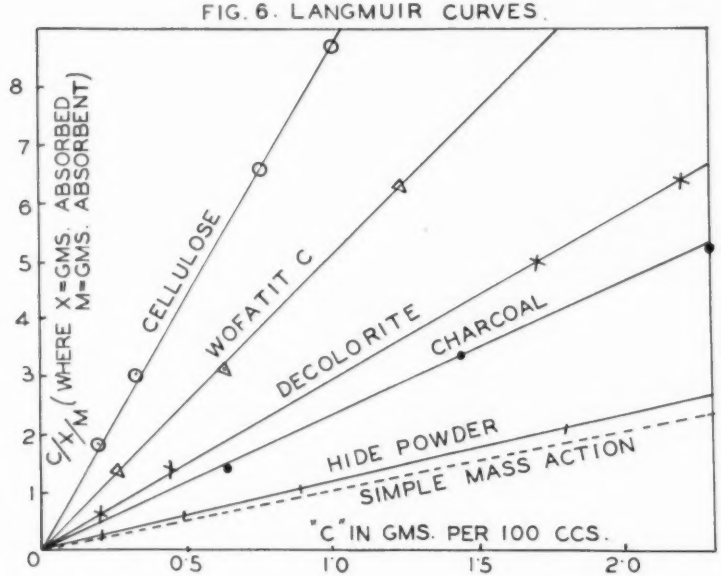
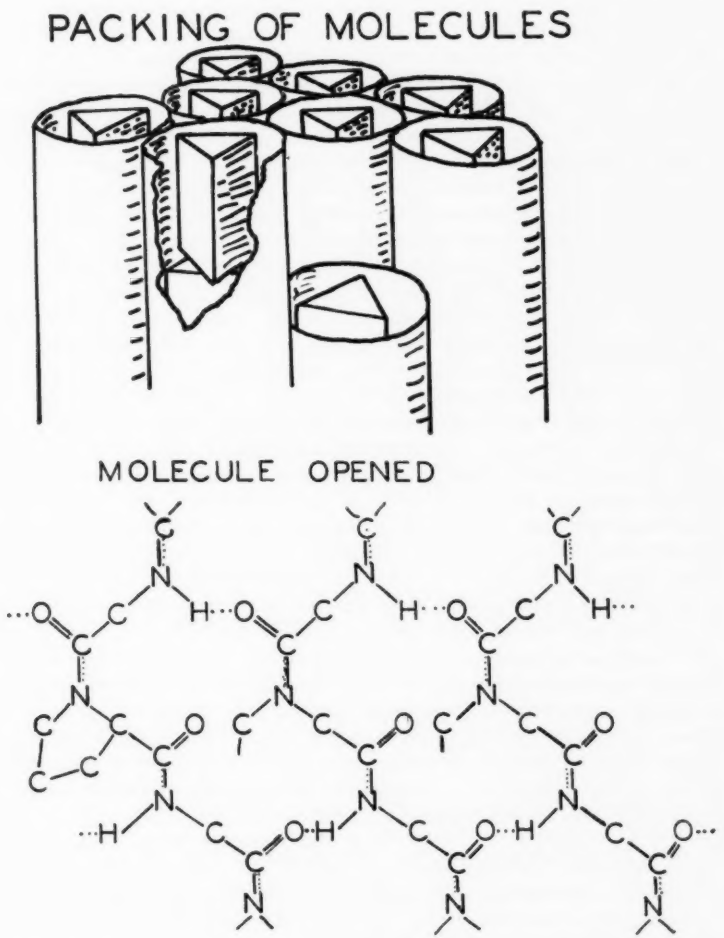


Fig. 7 is a reproduction of their model, and a protein fibre can therefore be considered geometrically as a large number of long cylinders each containing three polypeptide chains. These long cylinders are linked to each other laterally by salt links between the side chains which project in all directions from the cylindrical molecules. In aqueous solution these cylinders will be covered with water molecules hydrogen bonded to the hydroxyproline groups and the polypeptide backbones. Water molecules will also be attacted to the –COOH and $-NH_2$ groups on the side chains whether or not they are charged. This will constitute the "bound" water, and the free water will occupy the remainder of the space between the cylinders and side chains. In acid or alkaline solution the Donnan effect will draw additional water between the cylinders, forcing them apart, and thus causing two dimensional swelling. The two dimension nature of the swelling has been commented on by Stubbings and Theis[13] whose stratographic examinations of swelling of hides have shown that the hide fibers swell in thickness and not in length, so that the vertical fibers in the center of the hide contribute very little to the increased thickness of the hide, the latter being due mainly to swelling of the more horizontally disposed fibres nearer the grain and flesh surfaces. If tannage involved single fibers only, it is apparent that the maximum separation of the molecular cylinders prior to tanning would give the large tannin mole-

FIG. 7. STRUCTURE OF COLLAGEN



cules the optimum opportunity to reach all the sites on the cylinders and their side chains capable of hydrogen bonding to the tannin molecules. According to the model of Pauling and Corey (loc. cit.) the polypeptide chains

of a collagen molecule are arranged so that each– $\begin{matrix} N & - & C \\ | & & \| \\ H & & O \end{matrix}$ – group is conveniently situated to hydrogen bond to another, so that the molecule is able to link up most of its peptide group hydrogen bonds internally within the three chains constituting each molecule, leaving the hydroxy proline groups of the main chains plus side chain and amide groups free to hydrogen bond, plus peptide groups of the less well organized parts of the molecule. If the tannin molecules are able to penetrate along the surfaces of the cylindrical molecules of the organized parts of the protein and to approach the hydrogen bonded peptide groups sufficiently closely to compete for hydrogen bonds, some disorganization of the molecules would result. The fact that the X-ray diagram is not seriously altered by vegetable tanning suggests that this does not normally occur to any great extent. In practice the protein is not in the form of an unrestricted single fibre, so that the tannin molecules must be able to diffuse between the fibres of the hide or skin, and thence into the fibers themselves. Thus there must be an optimum acid and salt concentration for each tanning material to give this condition.

A second stereochemical factor is the tendency for the large tan molecules to become fixed in the outer layers of the cylinders comprising each fibre, thereby blocking the entry of other tan molecules. In the case of swollen fibres the spaces between the fibers may become so small that they are blocked by tan molecules which cross link and set the surface channels, thereby preventing penetration into the centre and resulting in the well known practical phenomenon of "case hardening". The use of small, more loosely held tannins or non tannins in the early stages of tanning would thus seem to be a method of preventing the early blocking of the channels through which the tannins must pass to reach the surfaces of the internal cylinders.

In regard to the choice of acid to produce the optimum amount of swelling, the organic acids are likely to be preferable to mineral acids for two reasons. In the first place they are capable of hydrogen bonding and hence filling a role as non tannins which promote passage of tannin molecules into the fibres. In the second place they have a buffering effect which tends to maintain a reserve of acid in spite of fluctuations in residual alkalinity carried forward by the hides from the lime pits.

Tanning Mechanism of Natural Vegetable Tannins

The above experimental work and theoretical considerations lead logically to the general conception of all naturally occurring vegetable tannins being large molecules capable of multipoint hydrogen bonding. These are surrounded by solvent molecules (usually water) hydrogen bonded at numerous points over the surface of the molecule, thereby rendering them compatible with the solvent as a whole. The protein molecules, though insoluble for

structural reasons, are also capable of multipoint hydrogen bonding, the chief sites being the $-NH-\overset{\overset{\vdots}{O\cdots}}{\overset{\|}{C}}$ groups, the hydroxyproline groups, and the side chain amino and carboxy groups. In aqueous medium the protein molecules are separated by both hydrogen bonded and free water to an extent depending on the swelling. The tannin molecules diffuse along the protein molecules and become hydrogen bonded to the protein, the firmness of fixation depending on the number of points and bond strengths of the attachment. This theory provides adequately for all grades of attachment of tannin from very firmly fixed to "combined water solubles", and for solvent tannage and solvent stripping. Also the multipoint attachment provides bridging between protein molecules which accounts for the reduction in swelling of tanned leather.

In the case of the condensed tannins or phlobotannins, the absence of carboxy groups makes an electrovalent mechanism impossible, except at pH values above 7.0, where the effect has been shown to reduce tan fixation. In the hydrolysable tannins, these appear to be mainly glucosides[14] with relatively few free carboxy groups, most of which will not be ionised at pH 3.0 where tan fixation is high. Thus, although electrovalent forces may play some part, the mechanism is again predominately a hydrogen bond mechanism. In both cases the molecules are capable of multipoint hydrogen bond attachment, and in solution will be surrounded by bonded water molecules, so that the operation of these adsorption mechanisms which depend only on the mutual cohesion of lyophobic molecules or their joint expulsion from the solvent system must be discounted.

Tanning Mechanism of Synthetic Tannins

The experimental work has been confined to a maphthalene sulphonic acid syntan, which has been shown to possess strongly lyophilic sulphonic acid groups, which drag into solution a large lyophobic molecule. Tanning is mainly a stoichiometric reaction between the acid groups and the protein side chain amino groups, with a small additional uptake which may be due to the presence of lyophobic carbon chains along the protein side chains which adsorb the lyophobic part of the syntan molecule. This is not considered to be adequate to explain reduction in acid swelling of the tanned protein, but instead it is suggested that multivalent ions reduce swelling through not being able to occupy positions simultaneously adjacent to all their oppositely charged protein side chain counterparts.

It is evident that it is possible to conceive of syntans occupying the whole field between naphthalene sulphonic acid and wattle tannin, i. e. with mechanisms which may be (a) entirely electrovalent, (b) partly electrovalent and partly adsorbtion, (c) partly electrovalent and partly hydrogen bonding,

and (d) entirely hydrogen bonding. Marked differences in leather properties and yield may be expected as types (a) and (b) will not only combine almost entirely with the side chains but will also tan mainly at low pH values, while types (c) and (d) will have a much broader tanning range and a far more multipoint attachment. The true "replacement" syntans are likely to be in category (d).

Lignin Sulphonic Acid

This paper would be incomplete without some consideration of lignin sulphonic acid. Lollar, Buchanan and Niemeyer[15] have found that the tanning properties of the lignin sulphonates are influenced by the type of wood (i. e. the type of lingin) and the cooking conditions, and can be correlated directly with their precipitability with high molecular weight amines. Kremen and Lollar[3] have shown that the presence of the free amino group of collagen exercises a substantial influence on the fixation of lignosulphonates, but is of slight importance with quebracho. Myrobalans is noted to be intermediate. The pH effect of tannage was significant. Whereas the degree of tannage of quebracho changed from 79.2 to 67.8 in changing from pH 3.75 to 6.0, that of magnesium lignosulphonate fell from 49.6% to 33.3%, while "Rayon Cook" lignosulphonate changed from 44.8% to 24.6%. Subsequently Lipsitz, Kremen and Lollar[3] have shown that certain magnesium lignosulphonates could give leathers of similar chemical analyses to the other tannages, but the leathers were more sensitive to tryptic digestion than quebracho and wattle tanned leathers.

From these results it seems evident that the tanning action of lignosulphonates is partly electrovalent and party either hydrogen bonding or adsorptive. In order to improve their suitability for tanning, Lipsitz, Lollar and O'Flaherty[16] have suggested the introduction of more hydrogen bonding units into the molecule, a suggestion which we endorse fully.

Summary and Conclusions

1. The vegetable and synthetic tannins are organic compounds of large molecular weight which would normally be completely insoluble in water except for the presence of lyophilic groups.

2. If the lyophilic parts of the tannin molecule are attracted to or held by receptive sites on a third component added to the tannins+solvent equilibrium, the equilibrium will be moved towards reduced solubility. Forces of attraction may be electrovalent, hydrogen bonding or adsorption.

3. Electrovalent forces promote solubility of ionised tannin molecules only, and at pH 3.0 will be confined mainly to sulphonic acid syntans, as the number of ionised groups per molecular weight aggregate is one per million for wattle tannin and one per 45,000 for tannic acid.

4. Hydrogen bond forces are responsible for the high solubility at low pH values of all natural vegetable tannins, the molecules of which are surrounded by hydrogen bonded envelopes of solvent.

5. Adsorption forces are considered to be of negligible consequence in a system lavishly endowed with hydrogen bonds, but important in molecules which are largely lyophobic, these being likely to be adsorbed mainly on the lyophobic parts of protein side chains, and unlikely to compete successfully with hydrogen bonded water on the lyophilic protein sites.

6. Comparative experiments with various adsorbents at different pH values show striking differences between wattle tannin and naphthalene sulphonic acid syntan, and confirm the opinion that the mechanism of tannage of wattle tannin is entirely hydrogen bonding, while that of the naphthalene sulphonic acid syntan is almost entirely electrovalent. Other types of syntan and also sulphite cellulose are considered to have tanning mechanisms which are partly electrovalent, partly hydrogen bonding, and partly adsorptive. The true replacement synthetic tannin is considered to be one which is lavishly endowed with hydrogen bonds.

7. The marked increase in uptake of wattle at low pH values is shown to be due to increased accessibility caused by swelling of the protein or amino resin, as it was eliminated either by tanning in the presence of 5% salt or by a pretannage at pH 4.8.

8. The restriction of swelling of collagen by vegetable tannage is considered to be due to crosslinkage caused by multiple hydrogen bonds. In the case of sulphonic acid syntans and phosphoric acid, restricted swelling is believed to be due to electrostatic attraction of multivalent anions unable simultaneously to occupy adjacent positions to oppositely charged counterparts on the protein side chains.

9. The collagen model of Pauling and Corey (loc. cit.) is shown to fit well with the two dimensional swelling of collagen in acids and alkalis, and it is concluded that the need for tannin diffusion between fibres as well as into fibres requires an optimum acid and salt concentration for each tannin. The phenomenon of "case hardening" is evidently due to blocking of the narrow passages between swollen fibres, and the function is noted of small more loosely held tannins or non tannins in holding open these passages.

10. The advantages of organic acids rather than mineral acids for deliming are considered to be their greater buffering power, and their ability to hydrogen bond along the surface channels and thus assist penetration.

11. The various active sites of the protein and the varying amounts of cross linkage possible, are considered to be sufficient to explain the differences between fixed tans and combined water solubles.

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ABSTRACTS

Statuory Developments in the Field of Water Pollution Control. By C. M. Henderson. *Eng. Bull.*, **35**, No. 6 (Purdue University) 43 (1951). *Through Sew. and Ind. Wastes* **24**, 802 (1952). In a general way there are presented the conclusions of a study by the Division of Water Pollution Control, U. S. Public Health Service, and the Office of the General Counsel, Federal Security Agency, on pollution control laws in the various states. The common law and its limitations are discussed. The principal drawback to dependence on the common law is that final decisions must rest with the courts, which can engage in only limited advance planning. Proper uses of natural resources require planning by government agencies and statutes by legislative bodies. The earliest statutes took the form of prohibitions of certain types of polluting discharges. The next important class of statutes was designed for the protection of health. In this area, regulation progressed from prohibitive measures to the vesting of administrative discretion in a technically competent agency. A great number of miscellaneous statutes, directed in some instances toward the prevention of pollution for the protection of specific stream uses and in other instances toward the exempting of certain industries, resulted in confusing administrative responsibility in many of the states. This led to what is termed "the modern trend," in which all state agencies interested in water pollution are merged into one over-all policy board responsible for promulgating a single set of rules and orders to control the subject from the state administrative level. At present some 30 states have adopted comprehensive legislation of this type.

The over-all agency is charged with controlling pollution so as to permit waters to be put to the best possible use. Its principal tools are generally: (1) limitations of new pollution through requirement of permits for new or increased waste discharges and (2) adequate enforcement powers to clean up existing situations. Although most of the statutes enacted in the last decade conform to these principles, they vary widely on particular points from state to state. Model legislation for pollution control has been incorporated in a "Suggested State Water Pollution Control Act," which was developed by the Public Health Service and is sponsored by the Council of State Governments. In recent years there has been recognition that the pollution problem goes beyond state lines. This has led to the development of several basin-wide compacts for interstate cooperation in pollution control. J. F. W.

Standards for Treated Industrial Wastes. By F. B. Milligan. *Eng. Bull.*, No. 6 (Purdue University) 105 (1951). *Through Sew. and Ind. Wastes*, **24**, 804 (1951). The purpose behind the development of water quality standards (dilution, effluent quality, or stream quality standards) is to provide a tool for use in the protection of public waters. Treatment to abate pollution, one of the most important measures for stream protection, is cheaper at the source than the sum of the costs at the points of use. Treatment at the source likewise places the cost on the originator of the damage. Effluent standards are useful criteria, particularly in the early stages of stream clearance programs in heavily industrialized areas, if they are properly determined and are applied with due consideration of the categories of the stream involved. In the later stages of restoration, stream quality standards have a definite place. Dilution standards are not adequate, as they are only approximate and cannot be applied to all stream conditions. Following a review of effluent standards established by other state and regional groups, the author discusses the effluent standards used in Pennsylvania. Industrial establishments are required to provide treatment of their waste waters equivalent to that for sewage, based on careful study and investigation. Primary treatment of sewage is defined as the removal of practically all setteable solids and at least 35 per cent of the B. O. D., effective disinfection of pathogenic organisms, satisfactory disposal of sludge, and a final effluent suitable for discharge into the public waters. In addition, oils, greases, acids, alkalies, toxic, putrescible, taste- and odor-producing substances, and other substances inimical to the public interest in the receiving stream must be removed. Complete treatment of sewage is similarly defined, except that removal of practically all of the suspended solids and at least 85 per cent of the B. O. D. load is required plus effective disinfection. Intermediate treatment is defined in accordance with the need in each substance. Through the cooperation of industry committees with the state authorities, standards have been established for the wastes from milk processing plants; from oil, natural gas, and other wells; acid pickling liquors and metallurgical plants; and all wastes from pulp and paper mills in Pennsylvania. Similar standards are currently under development for the tannery and textile industries; eventually standards will be developed for all waste-producing industries in the state. J. F. W.

The Administration of Stream Pollution Prevention in Some States. By Harold E. Babbit. *Eng. Bull.*, No. 6 (Purdue University) 239 (1951). Through *Sew. and Ind. Wastes*, **24**, 809 (1951). The author reports his conclusions after visits to stream pollution control authorities in 26 states. Comments are offered and state laws abstracted and quoted to emphasize certain administrative trends. Administration of stream pollution prevention varies from state to state and in general is in a condition of flux. Variations in control in Massachusetts, California, Maryland, Connecticut, Virginia and Illinois are discused. The standard of streams, with New York State law as an example, is discussed. Sections of the law are quoted at considerable length. The role of interstate pollution control authorities

is discussed and a list of these is presented. The author discusses the attitudes toward pollution control that he found in talking with (1) enforcing authorities, (2) polluters (3) users of the stream, and (4) the general public. A recent trend in state legislation toward divorcing the control of stream contamination from the control of stream pollution is noted. The removal of pollution authority from the Board of Health in California to Regional Water Pollution Control Boards is commented upon in some detail with mention to similar situations in Maryland and Connecticut. In some states, typified by South Carolina, a water pollution control authority exists within the state health department. In summary of the 26 states visited, complete jurisdiction over all stream pollution is assigned to State Health Departments in 20 states, whereas in the 6 other states these departments have lost control of pollution not directly affecting the health of the people. J. F. W.

Management's Approach to Waste Disposal and Stream Pollution. By Frank M. Shipman. *Eng. Bull.*, No. 6 (Purdue University) 324 (1951). Through *Sew. and Ind. Wastes*, **24**, 812 (1951). In presenting a comprehensive approach of industrial management to the problems of liquid wastes disposal and stream pollution the author selects five categories considered to be of major importance; *viz.*, (a) custom, (b) objective of regulatory agencies, (c) education, (d) cooperation, and (e) cost. Industrial establishments have been concentrated at points of vantage with reference to raw materials, sources of power, ease and economy of transportation, and availability of personnel; streams have been used for disposal of sewage and industrial wastes resulting from such concentrations and from congregations of masses of people in limited areas. The problem of the future resolves itself into (a) a practical approach to pollution correction by established municipalities and industries and (b) the prohibition of increased industrial activities in over-crowded areas. Cooperative effort is the essence of the successful approach to pollution abatement and control. Assistance to regulatory agencies by technical men of industry in wastes definition and evaluation is advocated. Industrial management has a definite responsibility of accounting in terms of a "dollars and cents" yardstick. Consequently, the cost of installations for prevention of stream pollution, as for installations pertinent to any phase of production, must be analyzed from the standpoint of economy. J. F. W

Discussion on Trade Waste (Tannery) Purification Plant. By W. Foster. *Jour. and Proc., Inst.* Sew. Purif., Part 2, page 98 (1950). Through *Sew. and Ind. Wastes*, **24**, 927 (1952). A description is given of a chrome tannery treatment plant in Scotland with a daily volume of 65,000 gallons, including 16,000 gallons (Imperial) of sulfide liquors from the liming process. The sulfide liquors were treated by aeration and the addition of copperas and then added to the main plant waste after the latter had been settled for 8.25 hr. This treated material was then discharged to the city sewers for further treatment with the sewage. Treatment results of the mixed effluent are given as follows:

	Before Treatment (p.p.m.)	After Treatment (p.p.m.)
Ammonia N	120	38
Albuminoid N	190	13.9
B. O. D.	600	320
Sulfides	480	46.3
Fats	46	18
Susp. Solids	7184	448

J. F. W.

Soil Conditions Are Affected by Tannery Waste Water. By C. R. Iyer, R. Rajagopalan and S. C. Pillai. *J. Indian Institute Sci.*, **34,** 163 (1952). A piece of agricultural land adjoining the area where waste waters from a tannery were impounded was steadily becoming infertile, although the soil was some years before fairly porous and fertile. The belt of land contiguous to this area maintained its porosity, friable texture, and its natural color and continued to be highly productive. This led to an investigation of the tannery effluents and soils, with conclusions as follows: The tannery effluents invariably contained high amounts of sodium chloride and also small amounts of chromium and arsenic. The vegetable liquors were the usual dark colored, odorous liquids. Soil from the affected belt contained large amounts of soluble salts, especially sodium chloride. The mechanical texture of the soil was adversely affected, especially with regard to pore space and water holding capacity. Sodium clay had formed and in consequence, the lime had leached out. The soil had become alkaline. Soils from the fertile belt showed none of these undesirable characteristics. It was evident, therefore, that the waste waters from the tannery were responsible for the deterioration of the soil.

Water Analysis. By S. K. Love and L. L. Thatcher. *Anal. Chem.*, **24,** 294 (1952). This constitutes the fourth annual review of analytical procedures applied to the analysis of water and reported in the technical literature. In this review a section is devoted to instrumentation, another section is given over to qualitative detection of trace elements in water, while a third section discusses advances in colorimetry applicable to water analysis. One hundred thirty-five references are cited.

Coatings. By T. G. Rochow and R. W. Stafford. *Anal. Chem.*, **24,** 232 (1952). This review of the literature of the past year on coatings covers advances in chemical and physical analytical methods applicable to organic high polymers and associated oils, waxes, pigments, and plasticizers. General analytical schemes are considered first. The next section is devoted to the generally applicable resinography and related topics, the fundamental importance of which is evidenced by the increasing activity in this field. Monographs on the analysis of component parts of organic coatings are then considered in the order: separate classes of resins oils, waxes, pigments and plasticizers, and specific constituents or functional groups. Auxiliary references to a limited bibliography on relevant descriptive or evaluative literature are presented as generally helpful background information. A total of 158 references are cited.

Solid and Gaseous Fuels. By H. T. Darby. *Anal. Chem.*, **24,** 244 (1952). This constitutes the third review of the analysis of solid and gaseous fuels. It covers the literature from September, 1948 through September, 1951. It discusses the sampling, testing, and analysis of such fuels as coal, coke, wood charcoal, and briquets. One hundred twenty-nine literature references are given.

Tanning Machinery in Practice. III. By C. Hall. *Lea. Trades Rev.*, **99,** 131 (1951). The reasons for the failure of tannery machinery to perform satisfactorily or to withstand wear are discussed.

East African Hides and Skins Industry. Assessing the Value of Air Drying Processes. By M. H. French. *Lea. Trades Rev.*, **99,** 333 (1951). Hides or skins dried over poles were found to damage where pole and hide contacted. Hides dried on frames or

in sheds were equally well preserved, however, since frame drying conditioned the hides in a shorter period of time, this method produced less hair slip and is to be preferred in the rainy season. The author summarizes his observations as follows: "Shed or suspension drying permits a more uniform rate of dessication and allows sufficient time for moisture from the central layers to move to the surface and evaporate before the outside layers become case-hardened. Recent experiments in Nigeria have indicated that the rapid drying of property suspended hides does not result in grain cracking. When pegged out on the ground the upper surface of hides and skins is rapidly dried by the sun and, because of changes in the nature of the surface proteins, become case-hardened. Under such conditions a central layer can be enclosed, within the dry surface layers, which may remain moist for a long period after removal to the store. This moist layer can serve as a fertile medium for bacterial action for a long time after the hides and skins are apparently quite dry. Bacterial damage of this nature can lead to a separation of the outer layers of the pelt in the beamhouse, a defect which is known as sun blister. When pegged on the ground the hair side is in actual contact with the ground and drying of this surface may, therefore, be retarded sufficiently to allow bacterial action to take place. This results in damaged grain, eroded patches and even holes through the substance. When pegged on the ground there is considerable danger of over-drying, which can alter the fibril structure so that its ability to absorb water is permanently impaired and the fibrils are unable to resume their natural crinkly character. At the same time the intra-fibrillary proteins and any collagen degradation products are denatured and converted into insoluble cements. This, of course, interferes with their subsequent removal in tanneries and reduces the value of the resultant leather. With pegging in the sun a thin parchment-like film may form over the flesh surface of the drying hide or skin. During the subsequent tannery processes this membranous film does not swell easily in water, causes difficulties during fleshing and also retards the penetration of water, lime and tannins, etc., into the pelt. When pegged on the ground little cooling can take place and the temperature of the drying hide or skin may rise considerably. As is well known, heat and moisture are ideal conditions for the conversion of collagen into glue, and it is possible that this chemical action takes place and adds to the damage done by putrefactive organisms. Even when hides and skins are suspension dried, it is essential to remove fat and the larger lumps of meat from the flesh side. This is because the lumps retard drying and encourage putrefactive damage in the underlying hide substance. If superfluous lumps of fat are left on a hide which is pegged on the ground the sun's heat may cause a rupturing of the fat cells, so that the freed fat can seep over the surface and into the hide substance. This free fat will retard drying over a larger area than that immediately below the lump of fat while the freed fat is more readily hydrolysed or oxidized to a rancid condition with the liberation of fatty acids.

The Tanning and Dressing of Sheepskins. *Lea. Trades Rev.*, **99**, 135 (1951). The two principal uses for sheepskins are for tanning into basils and roans and for splitting in the limed or pickled state for skivers and fleshes for chamois and washable glove leathers. After pickling, sheepskins are degreased by drumming in 50 per cent warm paraffin with the addition of 1 per cent surface active agent for 2 hours, followed by fleshing and washing in warm brine. They are then degreased before or during tanning, or solvent degreased in the crust. Basils are drum tanned in two days or paddle tanned in a week. A blend of mild vegetable tannins is used. Skins oiled and dried are known as crust basils. The basils are then sorted according to the use to which they will be put, dampened, shaved, stripped with borax or sodium carbonate, soured or bleached with oxalic acid or acid syntan, retanned with vegetable tannins or dyed, fatliquored and dried. Natural leathers are rolled. Glazed leathers are sprayed with casein or albumin, bound finish, then with formaldehyde to fix the

finish, and glazed. Smooth finish basils are sprayed with a casein wax bound finish or with a synthetic resin emulsion and plain flat plated. Fancy embossed basils are sprayed with synthetic resin bound finishes, embossed, and often fancy lipped with shellac. The chief requirement of hat leathers is resistance to perspiration.

Myrobalams: Indian Methods of Production. By B. Wilson, *Lea. Trades Rev.*, **100,** 605 (1951). The myrobalam tree grows in the jungle forests of India and is most prolific in the Central Provinces. Other important areas are the Rajapore and Bhimli districts. The fruit bears from April to May onwards and is mature towards the end of September, when it falls from the tree. The jungles are the property of the government and every few years are auctioned to the highest bidder, the lease running from 3 to 10 years. A lessee may control an area of 500 square miles, has his established collecting centers outside the jungle and adjacent to road or rail. He relies on casual labor or native dwellers to collect the nuts. At the nearest established sorting and crushing center the nuts are handpicked and graded. Crushing is hand work also, carried on principally by women. There is agitation on the part of the importer to screen and sieve the crushed nuts, thus precluding dust and foreign matter from bulk shipments.

Trade Wastes and Their Treatment. *Lea. Trades Rev.*, **100,** 65 (1951). Before tannery effluent enters the town's sewers, or is discharged to rivers or streams, certain preliminary purification treatment is often necessary. It is suggested that this consist of three steps, namely: (1) collection of waste liquors into a suitable tank or series of tanks, (2) sedimentation or addition of coagulant and sedimentation, and (3) filtration. Limes and soaks present the most serious problem in effluent purification.

Production of Chrome Retan Leathers. *Lea. Trades Rev.*, **100,** 597 (1951). Tanners in Great Britain have heretofore avoided the use of vegetable tanning agents, except mordants, on chrome leather. It has been found, however, that it is possible to tan lightly with chrome, and then retan with a syntan or a combination of syntan and vegetable tannin. The leather should contain about 2.5 to 2.7 per cent Cr_2O_3. Chrome tanning is followed by approximately 2.5 per cent syntan, and retannage completed with myrobalams and wattle. A fuller, mellower leather is thus obtained.

Renovation Processes for Leather Goods. By A. J. E. Moss, *Lea. Trades Rev.*, **100,** 599 (1951). Directions are given in detail for the cleaning of leather clothing, gloves, etc.

Fighting the Menace of the Warble Fly, I. German Methods and Experiments. *Lea. Trades Rev.*, **102,** 371 (1951). A select committee of the Committee for Hide Improvement met in February, 1951 at Wiesbaden with representatives of the Ministries of Agriculture, Food and Forests, and scientists concerned with cattle disease and insect damage. Walter Freudenberg reported on the fight against the warble. Dr. Schmidt, Essen, reported that chemical treatment had almost superceded mechanical treatment by hand. Dewarbling before turning cattle out to pasture had proved insufficient as warbles emerge as late as September. R. Goetz reported that the warble fly damaged not only leather, but the health and development of the cattle. Young animals with more than 12-20 warbles were slow in growth; milk cows with more than 20-30 warbles gave less milk; warbles wandering through the back of young cattle might cause spinal disease. Large numbers of Hypoderma lineatum gathering in the vicinity of the throat might cause paralysis or inflammation of the

aesophagus. Festering of warble lumps were the cause of painful inflammation of the hide. Warble allergies further killed or damaged a large number of cattle with or without dewarbling. Pains should be taken to kill warble flies out of doors or when it is depositing its eggs. The best dewarbling period is considered to be mid-February until September. Hides with less than 10 warble lumps can be hand treated but above this number they should be washed with a good derris root infusion. R. Kuhl reported that D.D.T. spray was ineffective. Dr. Enick, Hamburg, examined the efficiency of several insecticides and disinfecting agents. The washing method of application was used. The drugs used contained colloidal sulfur. Materials used were Dekaseptol, an emulsion containing carbon disulfide and chloroform; Jacutin, a hexachlorcyclohexan; Sebacil, containing an organic thiosulfate; Derrilavol, a derris drug. The derris drugs penetrated particularly well. The other products were not quite so successful as those containing derris. Prophylactic treatment with Jacutin was preferred to D.D.T. Frequent change of pasture land, sprinkling pasture with Nexit, isolation of the pasture by means of cropland were tried without success. It was reported that some districts may be free of warbles because of certain undefined natural conditions, and it is suggested that these be investigated.

Fighting the Menace of the Warble Fly. How It Is Being Eradicated in the Netherlands. *Lea. Trades Rev.*, **102,** 597 (1951). Compulsory eradication of the warble is based on the rules of the Health Service and on legal regulations. These include the prohibition of bringing cattle with warble swellings to pasture and the obligation of killing as many larvae as possible if the cattle in the pasture are already infected. In April, all yearlings and heifers that have palpable swellings on their backs are treated. In May they are again treated. In June the older cattle are treated in the pastures, if necessary. Powdered derris or lonchocarpus root, suspended in water, is generally used for the foregoing purpose. The liquid is applied to the back with a medium hard brush so that the openings in the skin are freed. The treatment is successful, the larvae dying within five days, after which they dry up and fall from the skin in about a month. The average cost for each treated animal is 55 cents. In 1946 an average of 25 swellings was found for every young animal in the province of Utrecht: in 1947, 15; 1948, 10; 1949, 5; 1950, 4; 1951, 2, and many herds were entirely free from larvae.

Italy's Report on the Struggle Against the Warble Fly. *Lea. Trades Rev.*, **102,** 599 (1951). The Italian commission has concentrated its work on the study of the cause of the diffusion of the warble fly in Italy and publicizing this work with the aim of seeking government intervention for the obligatory dewarbling of cattle. This intervention has not been forthcoming because of lack of funds. The commission in the meanwhile recommends the voluntary destruction of the larvae.

Modern Practice in Leather Finishing IV. Testing the Properties of a Binder. By W. O. Nutt. *Lea. Trades Rev.*, **104,** 71 (1952). A film of binder dried on a glass plate is useful in assessing the characteristics of the material. Casein films which are tough yet brittle are usually suitable for glazing binders. If the film can be cut without breaking, the binder is more suitable for finishes. A well plasticized nitrocellulose is perfectly clear. Clarity of the deposited film will often reveal incompatibility in other binders too. The incompatibility of acrylic and glyptal resins is very easily seen by this method. Stability of a binder to mixing, alterations in pH, and compatibility with other binders, can be ascertained by trial. Mechanical stability of a resin may be determined by rubbing it between two glass slides. Stability of a resin to dispersion to increase in solids content may be judged by pouring a

few drops onto a filter paper and observing the adsorption of the water phase relative to the deposition of the resin. Stability of a resin dispersion to changes in pH by the addition of weak acid or alkali. Stability to ageing can be ascertained by conditioning the coated material in a stream of warm air for 8 hours, then at a room temperature for not less than 24 hours.

Methods for Determining the Tan Values and Combining Values of Vegetable and Synthetic Tannins. By F. Stather and H. Herfeld. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 1, 32-46 (1949); See THIS JOURNAL **36,** 415. The tan value ("gerbwert") of a vegetable tannin is the quantity of material absorbed per 100 g. dry hide powder treated with an excess of the tannin under specified conditions. The combining value ("Bindungswert") is the quantity of material retained per 100 g. hide powder after washing as in the Wilson-Kern method. The authors point out that tan values and combining values, determined for the same material in different laboratories, may not agree because of differences in details of the procedure. The effect of varying the conditions of the determinations on the numerical values obtained was studied. Materials used were 4 commercial tannin extracts (spruce bark, chestnut wood, wattle, and valonia), 3 auxiliary syntans (Tanigans), 4 replacement syntans, and 3 lignosulfonate materials. Distilled water must be used for dissolving the tannin, and for washing the hide powder before and after tanning. The tannin solutions should be clarified by centrifuging rather than by filtering. Values obtained using a 500-ml. shake flask were 1 to 2 units higher than when a 250-ml. flask was used. Values obtained by continuous rotation at 38 to 40 r.p.m. were mostly 3 to 7 units higher for tan value, and 1 to 4 units higher for combining value, than those obtained by intermittent hand shaking. Rotation at 58 to 60 r.p.m. gave lower values than at 38 to 40 r.p.m. No reason for this latter difference is suggested, but the necessity of using a prescribed rotation rate is evident. The effect of time was studied by determining tan value and combining value for 3, 8, 24, 48 and 72 hours contact. Both tan and combining value increased with time. The differences between 24- and 72-hour values are relatively small (1 to 7 units for tan value and 2 to 5 units for combining value). The order of the 14 materials according to decreasing tan or combining values is the same for the 24- and 72-hour determinations, except for slight shifts for materials whose tan or combining values are nearly the same. Consequently there is no justification for a contact time longer than 24 hours. Considerable variation exists, between the different tannins and syntans, with respect to the ratio of the 3-hour to the 24-hour combining value. These ratios ranged from 0.63 for spruce bark extract to 0.88 for Tanigan Extra A. Since this ratio gives some information as to rate of tanning, determinations both at 3 and 24 hours are advised. Temperature must be regulated. The effect of temperature variation is quite different for different materials. Determinations were made at 2, 10, 20, 30 and 40° during the shaking period. Except for the 3 auxiliary syntans (which gelatinized at 30 and 40°), the combining values were nearly doubled by going from 2 to 40°. The effect is relatively small below 20°. Tan values increased with temperature for spruce bark extract, the 4 replacement syntans, the lignosulfonate products, and (slightly) for the 3 auxiliary syntans (to 20°), and decreased with temperature for chestnut, wattle and valonia extracts. A temperature range of 18 to 22° is prescribed. Weight differences between aliquots evaporated with and without further dilution were negligible. Conditions for washing the tanned powder must be specified and adhered to rigidly. The washed hide powder should be dried initially at moderate temperatures (half a day each at 40, 60, and 80°) and finally at 100°; immediate drying at 100° gives higher results. All the preceding tests were made with 7.5 g. tannin to 5 g. dry hide powder, in 250-ml. liquor, i.e., 3 per cent concentration. Determinations were made with 3.75, 7.5 and 11.25 g. tannin (3 per cent concentration) per 5 g. dry hide powder, and with

7.5 g. tannin at 2, 3, and 6 per cent concentration. Both tan value and combining value increased with quantity of tannin given, especially from 3.75 to 7.5, and most markedly for materials of high tan and combining values. Tan and combining values also increased with concentration (at constant tannin dosage); the increases in combining value were quite small. No reason was found for changing the prescribed dosage and concentration. *Revised procedure:* Prepare a tannin solution containing 6 per cent tannin, dissolving and cooling as in tannin analysis. Centrifuge 30 min. at 3000 to 4000 r.p.m. and decant. Weigh an amount of hide powder equal to 5.0 g. dry material into a filter bell, closed with silk bolting cloth. Pass 1 l. distilled water through the hide powder. Drain. Transfer quantitatively to a weighed 500 ml. shake bottle, and weigh. Add water to make 130 g. (= 125 g. total water). Add 125 ml. of clarified tannin solution and rotate at 38-40 r.p.m. at 20 ± 2°, for either 3 or 24 hours. Add the liquor in 25 ml. increments, from a pipet, at 15 min. intervals for the 3 hour determination, and at 1 hour intervals for the 24-hour determination. Transfer the tanned hide powder to the filter bell and drain through silk bolting cloth. Remove the filtrate and centrifuge as above. Pipet 20 ml. of the centrifuged filtrate and 10 ml. of the original tannin solution into weighed dishes, evaporate and weigh. Tan value = $(A - B) \times 12.5 \times 20$, where A and B are the residue weights from the original and spent solutions respectively. Transfer the last of the tanned hide powder to the filter bell with a wash bottle stream. Wash with 9 l. distilled water, at a uniform rate, for 12 hours at 20 ± 20°. The tanned powder must be submerged completely throughout (see *Collegium* 1939, 455). Drain, suck dry, transfer the hide powder quantitatively to a weighed dish, and dry for one-half day each at 40, 60 and 80°, and finally at 100° to constant weight. Combining value = $(C - 5.0) \times 20$, where C = dry weight of tanned hide powder. The 24-hour values obtained for tan values and combining values (second figures) were: spruce bark extract, 74, 52; chestnut wood extract 101, 61; wattle extract 105, 53; valonia extract 89, 45; 3 auxiliary syntans 40-56, 16-18; 4 replacement syntans 51-79, 32-58; 3 lignosulfonates 11-48, 27-30. H. B. M.

Methods for Fractional Salting Out of Vegetable and Synthetic Tannins. By Hans Herfeld. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 2. 21-30 (1952). The determination of the fractions of tannin precipitated at 1/3, 2/3 and complete saturation with NaCl, first proposed by Stiasny and Salomon (see THIS JOURNAL, **19,** 689 (1924) as a method of getting at the relative molecular sizes of different tannins, does not give concordant results in different laboratories unless the procedures used are alike in all details. The results are influenced strongly by the methods used for clarifying the original solutions and separating the precipitates formed on addition of salt, and by agitation after adding salt, but not by allowing the original solution to stand 24 hours either before clarifying, or after clarifying before titrating. Since nontannins consume $KMnO_4$ in the Lowenthal titration, blanks must be run on detanned solutions and subtracted from all the results. The preferred method for determining the fraction precipitated at different degrees of saturation is to treat 3 separate aliquots with enough NaCl to give 1/3, 2/3 and complete saturation respectively, separate the precipitates by centrifuging, titrate the decanted solutions, and obtain the precipitated fractions by difference. The alternate procedure whereby one solution is treated successively with differing amounts of salt, filtered after each addition, and the precipitates redissolved and titrated, gives very much lower results. Recommended procedure: Prepare a solution containing exactly 1 per cent tannin, dissolving and cooling as in ordinary tannin analysis. Cetrifuge 15 min. at 3000-4000 r.p.m. and decant. Add 11, 22 and 32 g. finely powdered salt respectively to 3 100 ml. aliquots in 250 ml. flasks, and rotate at 38-40 r.p.m. for exactly 1 hour. Centrifuge immediately for 15 min. at 3000-4000 r.p.m. and decant. Determine tannin in aliquots of 5 or 10 ml. of each decanted solution and in

the original solution by the Lowenthal $KMnO_4$ titration method. Detan 50 ml. of the original solution, and 50 ml. of each centrifuged, salt-treated solution by shaking 15 min. with 3.5 g. of dry, lightly chromed hide powder, and filtering. Determine the $KMnO_4$ consumption of aliquots of the detanned solutions, and subtract these values from those obtained for the corresponding solutions before detanning. If the corrected $KMnO_4$ titrations are *A*, *B*, *C*, and *D*, for solutions treated with 0, 11, 22 and 32 g. salt, then $(A - B)/A$ = fraction precipitated at 1/3 NaCl saturation, $(A - C)/A$ = fraction precipitated at 2/3 NaCl saturation, $(A - D)/A$ = fraction precipitated at complete NaCl saturation, and D/A = fraction not precipitated by NaCl. H. B. M.

Investigations on the Question of the Most Suitable Extraction of Spruce Bark. By H. Herfeld. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 1, 19-31 (1949). Previous work showed that addition of 0.6 per cent Na_2SO_3 and 0.6 per cent $Na_2S_2O_5$ (on air-dry bark) to the extraction water increased the tannin yield by 60-70 per cent without impairing the quality of the resulting leather. Larger additions of Na_2SO_3 and $Na_2S_2O_5$ resulted in decreased NaCl precipitation, tan and combining values, and the production of a tinny, less full leather. Attempts were made to replace Na_2SO_3 – $Na_2S_2O_5$ by syntans, lignosulfonates, or commercial emulsifying agents. Laboratory tests showed that no increase in tannin yield was obtained by adding up to 5 per cent of syntans or lignosulfonates during extraction (12 commercial materials tested), but addition of certain emulsifying agents resulted in tannin yields that approached those obtained with Na_2SO_3 – $Na_2S_2O_5$. In semi-commercial and full scale extractions, treatments with 0.3 per cent Na_2SO_3 + 0.3 per cent $Na_2S_2O_5$ + 0.25 per cent of Neomerpin, Smenol V, Cyclanon LA conc., or Sellasol E gave yields practically equal to those obtained with 0.6 per cent Na_2SO_3 + 0.6 per cent $Na_2S_2O_5$. When all the sulfite-bisulfite was replaced, by 0.5 per cent of these emulsifying agents, yields were 10 to 20 per cent lower. Purity, pH value, tan and combining values of the extracts, and degree of tannage and shrink temperature of calf leathers tanned with the extracts, were not materially affected by partial replacement of sulfite-bisulfite by these emulsifying agents. Use of emulsifying agents to replace half the sulfite-bisulfite resulted in less sludge formation, better compatability of spruce with replacement syntans, more rapid tanning, and production of leather of improved color and elastic properties. H. B. M.

Suitable Evaluation of Spruce Bark Extracts. By Hans Herfeld. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.*, No. 6, 76-84 (1951). Some extract manufacturers use too much sulfite, in order to get the maximum tannin yield. Laboratory tanning tests were made with 16 commercial spruce bark extracts, using both calf and cattle hide. Rate of penetration was followed, and the final leathers were analyzed. Results are compared with the analytical characteristics of the extracts. Very rapid penetration generally was associated with low degree of tannage, low combining value and low NaCl precipitation at 1/3 saturation, while excessively slow penetration was associated with high NaCl precipitation values. The following standards are proposed: *Maximum permissable values:* ash 9.0, Fe_2O_3 0.05, CaO 0.70 per cent (on dry basis), pH 5, sludge (24 hour standing) 1 per cent by volume in 1° Baumé or 2.5 per cent by volume in 5° Baumé solution, tintometer reading (red) 15; *minimum values:* purity 60, fraction precipitated at complete NaCl saturation 52, tan value (24 hours) 65, combining value (24 hours) 40. No limits are prescribed for organic and inorganically combined SO_3, but high SO_3 generally was associated with high pH and ash, and low combining and salt precipitation values. H. B. M.

Spruce, Pine and Alder Cones as Tanning Materials. By H. Herfeld and E. Zieger. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.*, No. 6, 65-75 (1951). Spruce cones, fully rip-

ened and freshly picked contained tannin 7.5 – 14.4 per cent (14 per cent H_2O), purity 71 – 83.5, tan value (24 hours) 82-90, combining value 59-63. Tannin yield was increased to 9.4 – 17.09 per cent by sulfite extraction. An objectionable gumming deposit was produced by concentrating the extract. Seeds, spindles, and scales contained < 1, 7, and 13 per cent tannin respectively. Unripe cones, and cones gathered from the ground were much lower in tannin. Alder cones (with stems) contained tannin 10.5 – 18.6 per cent; purity 67 – 83, tan value 81 – 86, combining value 54 – 59. Cones only contained 18.5 – 22.6 per cent tannin. Pine cones contained only 2.5 per cent tannin. Satisfactory leathers were produced, on the laboratory scale, with both alder and spruce cones. H. B. M.

Influence of Aging of Vegetable and Synthetic-Tanned Leathers on Their Fixed Tannin Contents. II. By F. Stather and H. Herfeld. *Ges. Abhandl. deut. Ledernists. Freiberg/Sa.*, No. 1, 47-9 (1949). In preceding work (THIS JOURNAL **30,** 49) the hide powder was rather lightly tanned, which might account for the large increase in fixed tannin that was observed on ageing. In the present work, 5 g. of dry hide powder was tanned 24 hours with a large excess (7.5 g.) of tannin, and combining value was determined at once, and also after drying the tanned powder at 40°C. for 3, 10, and 30 days. The materials tested included 6 natural tannins (raw quebracho, sulfited quebracho, chestnut, oakwood, valonia, and spruce bark extracts), 2 "Hansa" lignosulfonates, 1 auxiliary syntan, and 12 replacement syntans. In every case, except that of the auxiliary syntan, there was a marked increase in combining value after 3-day drying. The increases, as percentages of the combining value determined before drying, varied from 4 to 67 per cent for the replacement syntans, and from 10 per cent (spruce bark) to 58 per cent (valonia) for the natural tannins. The vegetable tannins and lignosulfonates gave further small increases in combining value on ageing 10 and 30 days, but the replacement syntans did not. The results for replacement syntans confirm observations made on aged commercial leathers. H. B. M.

Staghorn Sumac as a Tanning Material. By H. Herfeld and E. Zieger. *Ges. Abhandl. deut. Ledernists. Freiberg/Sa.*, No. 7, 48-65 (1951). Data is given for tannin content and purity of numerous samples of East German sumac *(Rhus typhina)*. Great variation exists between samples. For a good year tannin in leaves plus stems (14.5 per cent H_2O) varied from 17 to 25 per cent, and purity from 43 to 57, while for a very dry year tannin averaged only 11 per cent, and purity 42. All these samples were from one locality; another region produced samples containing 23 to 36 per cent tannin, purity 52 to 69. The central stalks on which the leaves are borne contain only about 5 per cent tannin, purity about 28; hence separation of leaves and stalks is desirable. The tannin content, and purity, is slightly higher for leaves that have turned red, but extracts of such leaves give leather of poor color. The leaves must be dried promptly to avoid loss of tannin through fermentation. Silo storage, with added mold preventative, results in large tannin losses. Quality is lowered by slow drying at elevated temperatures, but not by *flash drying* for 1 to 1.5 min. at 150°C. Extraction in the cold, or at 50°C., gave a product with highest tan and combining values 87-90 and 56-58 respectively, and produced leather of the highest degree of tannage (67-71), but only 54-61 per cent of the total tannin was extracted under such conditions. For normal extraction, first at 50°C., then at 100°C., followed by concentration in vacuum, the product gave tan value 80, combining value 50, degree of tannage of leather 67, tannin yield 85 per cent. Initial extraction at 100°C., or concentration at atmospheric pressure, yielded inferior products. Semi-commercial tanning tests with goat skins produced excellent leather, when the sumac was harvested before the leaves turned red, and when initial extraction was done at 50°C. H. B. M.

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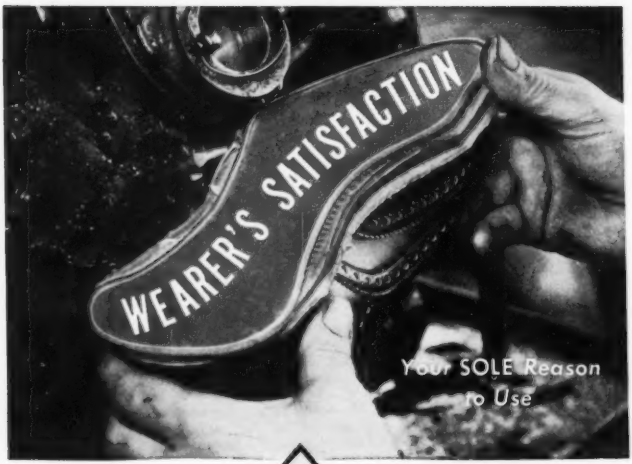

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